PB84-207638

Impacts of Coal Combustion on Trace Elements in the Environment: Wisconsin Power Plant Impact Study

Wisconsin Univ.-Madison

Prepared for

Environmental Research Lab.-Duluth, MN

Jun 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-207638

EPA-600/3-84-070
June 1984

IMPACTS OF COAL COMBUSTION ON TRACE ELEMENTS IN THE ENVIRONMENT

Wisconsin Power Plant Impact Study

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This study was conducted in cooperation with

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Madison Gas and Electric Company,
Wisconsin Public Service Corporation,
Wisconsin Public Service Commission,
and Wisconsin Department of Natural Resources

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U.S. ENVIRONMENTAL PROTECTION AGENCY
DULUTH, MINNESOTA 55804

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INFORMATION SERVICE
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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/3-84-070	2.	3. RECIPIENT'S ACCESSION NO. PB8 4 207638
4. TITLE AND SUBTITLE Impacts of Coal Combustion on Trace Elements in the Environment: Wisconsin Power Plant Impact Study		5. REPORT DATE June 1984 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) P.A. Helmke, W.P. Robarge, M.B. Schoenfield, P. Burger, R.D. Koons, and J.E. Thresher		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Water Resources Center University of Wisconsin Madison, WI 53706		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. R80-3971
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Duluth, MN 55804		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA-600/03

15. SUPPLEMENTARY NOTES

102 pages, 23 figures, 48 tables

16. ABSTRACT

The impact of a modern coal-fired generating station on the environment, with emphasis on the concentrations and behavior of elements and the disposal of fly ash, was determined by analysis of aerosolic dust, oak leaves, aquatic organisms, water, fly ash, and coal. The major analytical techniques used were neutron activation analysis, x-ray fluorescence analysis, atomic absorption spectrophotometry, electron microscopy, and x-ray diffraction.

Calcium, Ba, B, and Th concentrations were relatively high in the fly ash produced. When mixed with water, the fly ash reacts to form a cement-like material that includes pozzolanic mineral phases that were identified by x-ray diffraction and electron microscopy. Aerosolic dust collected in fallout buckets was enrined with Br, Hg, Sb, Se, Th, U, and Zn. Of the organisms tested, *Asellus racovitzai* and *Odanata* were most suitable for monitoring ecosystem trace element fluxes. Barium, Cr, Sc, and possibly Sb concentrations were higher in specimens of these organisms exposed to the ash effluent than in control specimens. These increases cannot be attributed to seasonal variability, sample contamination or differences in speciment size and are therefore thought to result from exposure of the organisms to ash effluent. Potential effects of fly ash from the Columbia Generating Station or other aerosolic dust on the concentrations of elements in oak leaves could not be detected.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Release to public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 113
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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FOREWORD

The U.S. Environmental Protection Agency (EPA) was established to coordinate our country's efforts toward improving and defending the quality of the environment. These efforts depend greatly on research to monitor environmental change and to determine health standards.

One project the EPA is supporting through its Environmental Research Laboratory in Duluth, Minnesota, is the study "The Impacts of Coal-Fired Power Plants on the Environment." The Columbia Generating Station, a coal-fired power plant near Portage, Wisconsin, has been the focus of all field observations. This interdisciplinary study is conducted by the Environmental Monitoring and Data Acquisition Group of the Institute for Environmental Studies at the University of Wisconsin-Madison and involves investigators from many departments at that same university. Several utilities and state agencies also are cooperating in the study: Wisconsin Power and Light Company, Madison Gas and Electric Company, Wisconsin Public Service Corporation, Wisconsin Public Service Commission, and Wisconsin Department of Natural Resources.

Burning coal to produce electricity releases chemicals into the air, soil and water around the Columbia Generating Station. The goal of the study described in this report was to determine possible changes in the environment surrounding the station. Aquatic organisms and oak leaves were studied to assess the bioaccumulation of trace elements in animals and plants that result from particulate fallout.

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ABSTRACT

The impact of a modern coal-fired generating station (Columbia Generating Station, Portage, Wis.) on the environment, with emphasis on the concentrations and behavior of elements and the disposal of fly ash, was determined by analysis of aerosolic dust, oak leaves, aquatic organisms, water, fly ash, and coal. The major analytical techniques used were neutron activation analysis, X-ray fluorescence analysis, atomic absorption spectrophotometry, electron microscopy, and X-ray diffraction.

The concentrations of Ca, Ba, B, and Th are relatively high in the fly ash produced. This is characteristic of ash from western coals like those burned at the Columbia Generating Station. When mixed with water, the fly ash reacts to form a cement-like material that includes pozzolanic mineral phases that were identified by X-ray diffraction and electron microscopy. The average flux of fly ash into the environment from the stack emissions was a few tenths of a $mg/m^2/day$ as measured by collection of aerosolic dust in fallout buckets. The aerosolic dust was enriched in Br, Hg, Sb, Se, Th, U, and Zn.

Of the aquatic organisms tested as indicators for monitoring ecosystem trace element fluxes, *Asellus racovitzai* and *Odanata* were the most suitable. The concentrations of Ba, Cr, Sc, and possibly Sb are higher in specimens of these organisms exposed to the ash effluent than in control specimens. These increases cannot be attributed to seasonal variability, sample contamination, or differences in specimen size and are therefore thought to result from exposure of the organisms to ash effluent. Corixidae, *Dineutus* spp., *Gammarus* sp., and *Hyallela azteca* were less useful indicator organisms. The contribution of the gut contents to the concentrations of elements in whole organisms is important for some elements in *A. racovitzai* and presumably in other taxons. A correction procedure must be used to remove the contribution made by the contents of the gut before elemental concentrations in whole organisms can be compared accurately.

Potential effects of fly ash from the Columbia Generating Station or other aerosolic dust on the concentrations of elements in oak leaves could not be detected. Grains of fly ash and other aerosolic dust are deposited on oak leaves. Their concentration on leaf surfaces increases through the growing season. This accumulation of dust causes concentrations of some elements in the samples to increase during the growing season, but all evidence indicates that these elements do not undergo bioaccumulation in leaves.

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SECTION 1

INTRODUCTION

The Columbia Generating Station, located on the Wisconsin River 4 miles south of Portage, Wis., consists of two 527-MW generating units. One unit started operation in April 1975 and the second in May 1978. Each unit burns about 4,535 metric tons/day (5,000 tons/day) of pulverized, low sulfur, subbituminous western coal which has an ash content of 7 to 8%. Columbia I, with a 150-m (500-ft) smokestack, burns coal from Colstrip, Mont.; Columbia II, with a 200-m (650-ft) smokestack, burns coal from Belle Ayr, Wyo.

High energy electrostatic precipitators were installed to reduce particulate emissions. Initially these precipitators collected 98% of the fly ash residue, but the addition of $NaHCO_3$ to the coal has increased their efficiency to the required 99.5%. The $NaHCO_3$ conditioner has been replaced with $(NH_4)_2SO_4$. Smaller particulate matter is released into the air. During the period when the electrostatic precipitators were operating at 98% efficiency, about 480 kg/h of fly ash were being emitted. This mass is equivalent to about 10 particles emitted/day (assuming 1 m diameter and a density of 1.65 g/cm). It is estimated that only 5 to 6% of the emissions from the stack reached the ground within 35 to 40 km. The fly ash collected by the precipitators for Unit I is discharged into an ash basin adjacent to the plant which uses replenishment water from the Wisconsin River. The fly ash from Unit II is collected dry.

Burning coal to produce electricity releases chemicals into the air, soil, and water around a generating station. The goal of the study was to determine possible changes in the environment surrounding the Columbia Generating Station. Two specific objectives were identified: (1) To measure the distribution and composition of fly ash and possible volatile materials in the area around the generating station and study the reactions and fate of fly ash in the environment; and (2) to study the availability of trace elements in fly ash to the biota. Procedures were developed to determine the amounts of trace elements originating at the generating station from trace elements derived from background sources.

To fulfill the first objective, samples of atmospheric particulate fallout were collected on the ground in buckets at various distances from the power plant and examined every month. Using an electron microscope, differences in shapes of the particulate material were determined. "Soil dust," which is angular, can be recognized as non-fly ash; this constitutes a substantial proportion of the fallout. Fly ash from other power plants or other sources in the region is pitted because it has traveled. Fly ash from local sources had a smooth surface and a unique composition at the time of the study. Thus, from the number of grains counted, it is possible to determine the percentage of the total amount of material that is local fly ash. Samples of fly ash from the stacks of units I and II and from the ash pond were examined to provide information concerning the concentrations of certain elements in the fly ash and the patterns of release of these elements from the fly ash to the environment.

To fulfill the second objective, two studies were carried out to evaluate the availability of trace elements in fly ash to plants and animals. In an attempt to learn whether plant life in the area is affected by trace elements in the fly ash, samples of oak (*Quercus* spp.) leaves were collected from sites near the power plant and analyzed by neutron activation. Aquatic arthropods were analyzed by neutron activation to determine the uptake of trace elements from fly ash that seeped into the aquatic system through the effluent from the ash basin. The ash effluent drains into Rocky Run Creek, a tributary of the Wisconsin River, which borders the power plant site.

Aquatic arthropods were selected because they are usually abundant in the shallow streams of the study area, they are near the base of ecologically important food chains, and the individual species of this phylum cover a variety of types of feeders--detritivore, omnivore, etc.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Concentrations of Ca, Ba, B, and Th are relatively high in fly ash produced at the Columbia Generating Station. This is typical of fly ash produced from subbituminous western coals compared to fly ash from eastern coals. The fly ash from Columbia shows a basic pH when mixed with water. The bulk concentrations of most elements increase as the particle size of the fly ash decreases. Exceptions are the concentrations of Fe, which decrease, and those of Hf, K, and Se, which are almost constant. Mercury is present in very low concentrations.

The fly ash from western coals has a high concentration of Ca. This characteristic means that the fly ash can possibly be used as a liming agent on agricultural soils. Research to evaluate this possibility is being conducted by others. However, application rates are anticipated to be limited by the concentration of B. Other elements studied would not limit application rates. Research is needed to control fugitive dust during application and to retard the availability of free lime so that applications can be made less frequently and at higher rates.

Analyzing samples of aerosolic dust by electron microscopy distinguishes fly ash from other dust particles because fly ash particles are spherical. The flux of fly ash deposited into fallout buckets around the Columbia Generating Station was a few tenths of a mg/m /day over a period of 1 month. At the time of this study, the fly ash from the Columbia Generating Station could be distinguished from background fly ash on the basis of its distinct chemical composition. Analysis with X-ray fluorescence showed that background fly ash had concentrations of Si > Al, K > Ca, and detectable concentrations of S, Cr, Mn, Co, and Na. The concentrations of Si and Al were similar in the Columbia fly ash, Ca > K, and the other elements were present at very low or undetectable concentrations. The flux of fly ash in the fallout buckets from Columbia was usually < 10% of the total flux of fly ash except for those months that had a very high flux of fly ash because the plume fumigated the sample site. Over 80% of the total fly ash in the buckets was from Columbia under these conditions. The results from the samples collected in the fallout buckets show that the Columbia Generating Station has little effect on the composition of the aerosolic dust within several kilometers of the stack, except for the times when the plume touches down.

Concentrations of elements in the dust collected by the fallout buckets varies from month to month. Most of the elements in the dust are present at concentrations similar to those of the local soil. Elements present at significantly higher concentrations in the aerosolic dust are Br, Hg, Sb, and Se, and to a lesser extent Th, U, and Zn. Some of this increase may result from the effects of fly ash because fly ash has relatively high concentrations of Sb, Se, Th, and U. Additional studies are needed to determine if the addition of fly ash particles to aerosolic dust changes the properties of aerosolic dust and the way in which it interacts with other components of the environment.

Fresh fly ash consists mostly of glassy, amorphous material. Small amounts of quartz, anhydrite, magnetite, hematite, periclase, and CaO are present in the fly ash from the Columbia Generating Station. Several new minerals form in the fly ash after it is mixed with water and slurried to the ash pond. The most important of these are the calcium aluminate sulfates and calcium aluminate silicates. These minerals contribute significantly to the strength and properties of Portland cement; the hardness of the fly ash in the ash pond must result from these minerals. Future research should explore the pozzolanic reactions of fly ash so that new uses of fly ash can be developed. These reactions also may be useful in reducing SO_4 pollution in other wastes because the calcium aluminate sulfates are much less soluble than gypsum.

The concentrations of soluble Al, Ba, Ca, and Cr as CrO_4 are much higher in water from the ash pond and its drainage system as compared to unaffected waters. Some of the CrO_4 is reduced to Cr^{+} in the lower portions of the ash pond drainage system where it precipitates as $Cr(OH)_3$. Also, $Al(OH)_3$ precipitates as the pH decreases to more neutral values. The system is saturated with $BaSO_4$. All of these materials coat the substrate of the drainage system. The presence of these precipitates may disrupt the habitat and life cycles of aquatic organisms that inhabit the waters.

Of the elements studied, the concentrations of Ba, Cr, and Se were significantly higher in aquatic invertebrates taken from the drainage system of the ash pond than in paired samples from unaffected streams. The concentrations of Se were 10 to 20 times greater than those found for control samples. These trends were most easily measured in samples of *Asellus racovitzai*, but they were also identified in samples of *Hyallela azteca*, and Odonata. The analytical samples of organisms were contaminated by ingested sediment. Samples of *Dineutus* spp. were contaminated to an intermediate extent; *A. racovitzai* was the most contaminated. These levels of contamination correspond to the amount of ingested sediment expected: the least contaminated, *Dineutus* spp., feed on the water surface; Corixidae and *Gammarus* spp. are herbivorous, *A. racovitzai* are benthic detritivores. A procedure was developed that compares the concentrations of individual elements to the concentration of Sc in samples of organisms and their casts. Interelement concentration ratios that provide a basis for correcting the analytical results for the effects of this contamination can be obtained from this procedure. The concentration of elements also varied within a species according to specimen size and date of collection. These factors had to be normalized in order to determine the effects of the effluent of the ash pond on elemental concentrations in aquatic organisms.

The experience gained in this research shows that aquatic invertebrates are useful in showing biological uptake of elements. To be useful as indicators of elemental fluxes in an ecosystem, the organisms selected for study should: Be amenable to collection and analytical techniques; be widely distributed throughout the study region; be present at the site of collection long enough to reflect the element conditions at the site; be relatively common to the habitat encountered at the study site; be able to tolerate a wide enough range in water quality so that the organisms will not be killed, except under very stressful conditions; have measureable elemental concentrations that can be correlated with environmental conditions; and have elemental concentrations that have a relatively small sample standard deviation to preclude the necessity of performing many analyses.

Particles of fly ash and other aerosolic dust are visible on samples of oak leaves when they are viewed with an electron microscope. Most of the particles are not removed by washing the leaves. Experiments with radioactive tracers of Eu, Hf, Sc, and Tb show that the uptake of these elements by young oak trees is small. The uptake of Sc is insignificant. Since Sc is present at relatively high concentrations in fly ash and aerosolic dust, this element was used in a procedure based on interelement concentration ratios. This procedure was used to correct the analytical results of the oak leaf analyses for the effects of dust contamination. The concentrations of potentially toxic elements of interest in this study--As, Sb, Se, Hg, Th, and U--were low or below detection limits in oak leaves. Seasonal variations in the concentrations of many elements were reproducible from year to year for leaves from the same trees. No effects of aerosolic dust or fly ash on elemental concentrations in oak leaves were found, although particles of fly ash were present on the leaves. Possible physical effects of alkaline or acid particles of fly ash on leaves should be investigated.

SECTION 3

MATERIALS AND METHODS

COAL, FLY ASH AND AEROSOLIC DUST

Samples of coal and fly ash from each of the stages of the electrostatic precipitator were analyzed by neutron activation and x-ray fluorescence to determine the partitioning of elements during combustion. Samples of fly ash collected from the base of the stack were analyzed to estimate the composition of the fly ash emitted to the atmosphere. Distribution of particles according to size was determined by electron microscopy. Samples of fly ash from the ashpit were studied to determine the devitrification and recrystallization of fly ash in the environment. Samples of aerosolic dust collected in fallout buckets were studied to determine the distribution and composition of aerosolic dust and fly ash in the environment surrounding the Columbia Generating Station.

PROCEDURES AND METHODS

The electrostatic precipitators are located at the base of each stack. Each precipitator is divided into four gas flow sections (Figure 1). Each section is further sub-divided into eight compartments arranged with two across and four parallel to the gas flow. The material collected in each of the compartments can be emptied into individual hoppers and later transported to a collection point. Some of the fly ash goes to a storage facility from which it is sold for commercial uses.

For convenience, the individual sections in each gas flow section (insert in Figure 1) are labeled stages I through IV in the order in which the flue gas passes through them. Since each stage has a collection efficiency of 80%, the first three stages are responsible for nearly all the fly ash collected; the last stage, stage IV, is subdivided into smaller sections and collects only small amounts of ash. Samples of fly ash were stored in sealed glass jars.

Samples of fly ash from Columbia I were collected on four sampling dates: 5 September 1975; 22 April 1976; 7 February 1978; and 8 March 1978. Supplied by Wisconsin Power and Light Co. (WPL), these samples were collected from the hoppers beneath the gas flow sections of the electrostatic precipitators. For the 1975 sampling, a sample of bottom ash (slag) from Columbia I also was obtained. Two additional samples of Columbia I ash were obtained from a consulting firm which collected them during a testing program. Collected on 9 and 14 July 1976, these samples came from the flue gas at the base of the stack at a point where it had already passed through

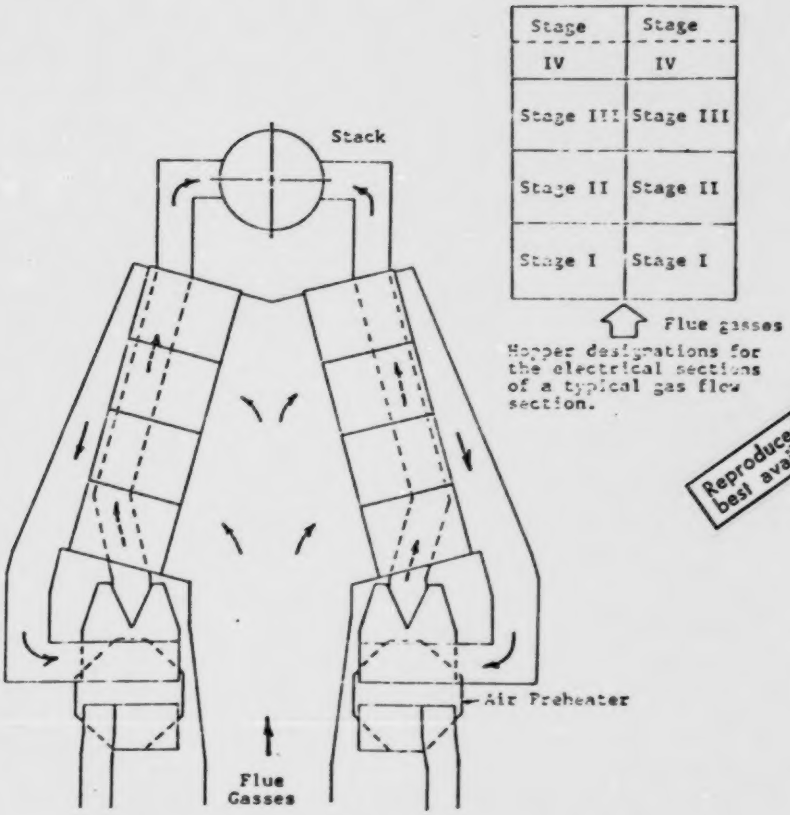

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Figure 1. The Columbia I precipitators and a typical gas flow section.

the precipitatiors. Only a single sample of Columbia II fly ash was obtained. Collected by WPL on 8 March 1978, this sample, was a composite collected from all four precipitator stages.

Fly Ash from the Ash Pit

Samples of fly ash were obtained from the ashpit by digging a pit. The fly ash was too hard to sample with an auger. All of the samples were from the upper 60 cm. The moist samples were sealed in glass jars for storage until analysis.

The suspended particulate matter in the ashpit and its drainage system were sampled by collecting several liters of water in clean plastic containers. The water was filtered through a 0.45-μm Millipore filter to collect particulates.

Samples of coal were obtained from WPL; these samples were portions of samples the utility collects for their routine analysis of S, heat content, moisture, etc. The samples, crushed to about 5-mm size when obtained, were ground to a fine powder in an alumina ball mill and stored in sealed glass jars. Samples of Colstrip coal were obtained from Columbia I for the coal burned on 3, 13, 26, and 27 May 1975 and on 8 March 1978. A sample of Belle Ayr coal from Columbia II was obtained for 8 March 1978. In addition, a composite sample of Belle Ayr coal from trainloads 132 through 185 that was burned during early 1978 was analyzed. A sample of Colstrip coal obtained by WPL in 1974 for evaluation purposes also was analyzed. Three samples of eastern coal from Illinois were analyzed in 1974 for purposes of comparing the results. They are: 3A-015 from the Elm Mine, Midland Coal Co., which is burned at the Edgewater, Wis. station; 3B-017 from the Fidelity Mine, United Electric Co., which is burned at the Nelson Dewey station, and 3C-018 from the Murdock Mine, Ziegler Coal Co., which is burned at the Rock River station.

Aerosolic Dust

Samples of aerosolic dust were collected in fallout buckets at six sampling sites (Figure 2). The collection date of each sample is given in Table 1.

The polyethylene collecting buckets, circular cylinders closed at the bottom and with an opening of 20 cm in diameter at the top, have a volume of approximately 2 liters. These buckets were installed in the field on top of metal poles so that they were situated approximately 2 m above the ground surface. Each bucket has a ring with a diameter of 30 cm around the top to prevent birds from perching and contaminating the sample. Efforts were made to keep water or snow in the base of each bucket to enhance the entrapment of particles. The buckets were sampled and collected monthly. This was done by replacing the dust buckets in the field with clean ones from the laboratory. In the laboratory the materials collected in the buckets were transferred--by washing--to a vacuum filtration unit from which they were collected onto either 0.45 or 0.1-μm Millipore or Nucleopore filters. The filters were weighed before filtration. After filtering the samples were

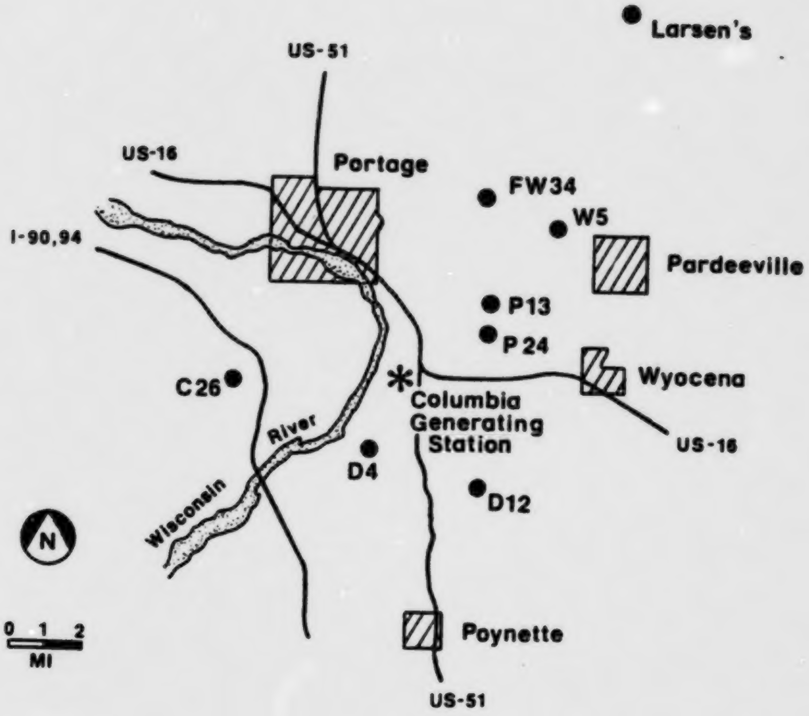

Figure 2. Sampling sites for the collection of aerosolic dust.

TABLE 1. SAMPLING SITES AND DATES OF COLLECTION FOR AEROSOLIC DUST SAMPLES[a]

		Sampling sites						
	Date	W5	C26	Larsen	P24,P13	D12	FW34	D4
1974	Nov.		x		x			
	Dec.	x	x		x			
1975	Jan.	x	x		x			
	Feb.	x	x		x			
	Mar.	x	x		x			
	April	x	x		x			
	May	x	x					
	June	x	x					
	July	x	x		x			
	Aug.	x	x					
	Sept.	x	x		x			
	Oct.	x	x		x			
	Nov.	x	x		x			
	Dec.	x	x		x			
1976	Jan.	x	x		x			
	Feb.				x			
	Mar.	x	x					
	April							
	May							
	June			x				
	July	x	x	x	x	x		x
	Aug.	x	x	x		x		x
	Sept.							
	Oct.	x	x	x	x	x	x	x
	Nov.							
	Dec.	x	x	x	x	x	x	x
1977	Jan.							
	Feb.		x	x		x	x	x
	Mar.							
	April				x	x		
	May							
	June							
	July	x	x					
	Aug.	x	x	x	x			
	Sept.	x	x	x	x			
	Oct.	x	x	x	x			
	Nov.							
	Dec.							
1978	Jan.							
	Feb.					x		
	Mar.	x	x	x				
	April							
	May	x			x	x		x

[a] See Figure 2 for site locations.

dried at 60°C and reweighed. The weight lost by the paper during filtering was determined for each batch and a correction applied to the measured mass of aerosolic dust.

Analytical Procedures

The samples of fly ash, coal (50 to 200 mg each), aerosolic dust, and particulates from the ashpit were analyzed by neutron activation procedures (Henzler et al. 1974, Koons and Helmke 1978). For samples of either aerosolic dust or particulates from the drainage system of the ashpit, the concentration of elements in the filter paper were low enough so that no blank correction was needed. Filtered water samples from the drainage system of the ash pond were analyzed by neutron activation; SO_4 and CrO_4 were done by nepheleometry and spectrophotometry, respectively. The major elements (Si, Al, Ca, Mg) were determined by x-ray fluorescence analysis. The mineral species were determined in the samples of fly ash from the ashpit by x-ray diffraction and electron microscopy.

The standards used for neutron activation analysis include standard soil SO4 from the collection of the Canadian Certified Reference Samples (Koons and Helmke, 1978), U.S. Geological Survey Cody Shale SCO-1, bovine liver and orchard leaves from the National Bureau of Standards, and liquid standards prepared from pure laboratory reagents (Henzler et al., 1974). The standards for X-ray fluorescence analysis and other analytical techniques were prepared from pure laboratory reagents.

The abundance of fly ash grains in the samples of aerosolic dust was determined by electron microscopy. For samples collected in 1974, the containers were opened after neutron activation analysis of the samples and a small (5 mm diameter) portion of the filter paper and samples were placed on an Al stub with double-sided tape. This often resulted in samples that were too dense with particles for easy visual analysis. For the later samples, a small aliquot (1 to 3 ml) was removed from the well-agitated suspension in the bucket and filtered separately on a Nucleopore filter for electron microscopy. The samples were coated with C in preparation for analysis.

Fly ash, the only spherical particles in the samples, are easily distinguished by electron microscopy from particles of soil, pollen grains, and other dust. To obtain a count of the relative number of fly ash and other grains in each sample, the microscope stage was moved back and forth and advanced at regular intervals; the grains were counted at each setting. A minimum of 1,000 grains/sample was counted.

AQUATIC INVERTEBRATES

The primary objective was to determine the effects of the ash effluent from the Columbia Generating Station on the concentration of elements in aquatic organisms, especially arthropods living in the drainage system of the ashpit. These organisms were selected because they are usually abundant in the shallow streams of the study area, they are near the base of ecologically important food chains, and the individual species of this phylum cover a variety of types of feeders; i.e., detritivores, omnivores, etc.

The selection of arthropods as the analytical specimens posed several additional questions which needed to be answered before the analytical results could be interpreted and the effects of the ash effluent determined. These include the effects of inorganic contamination on the elemental concentration in the organism (contamination due mostly to ingested sediments); the variability of elemental concentrations in the natural population of organisms that was sampled; and the effects of organism size, and other possible factors, on elemental concentrations. Suitable samples of selected species were collected, analyzed, and the results interpreted to determine the effects of these variables.

The general approach used to determine the effect of the generating station was to compare elemental concentrations in organisms collected before and after the Columbia Generating Station began operation in April 1975. Additional control samples were collected after the station began operating from nearby sites that were not affected by the ash effluent. Several species were studied initially to determine their suitability for this research. One species was selected for more intense study. In addition to providing information on the bioavailability of elements in the ash effluent, the results presented can form a base for future studies that assess the effects of elements on the behavior of organisms.

Site Description

The organisms were collected in the vicinity of the Columbia Generating Station, Columbia County, Wis. This facility is located on the floodplain of the Wisconsin River. This section of the state consists of glaciolacustrine deposits modified by fluvial action and surface weathering overlying sandstone bedrock. The sampling sites are shown in Figure 3. Samples were collected and analyzed from 1974 through 1978. Specific sampling dates and locations for each sample of organisms analyzed are presented in tabular form later.

The influence of the ash effluent on elemental concentration should decrease with increasing distance from the basin due to settling of suspended particulates and dilution of dissolved and suspended materials. These processes should decrease the concentrations of waterborne substances. The ashpit basin, ashpit drain, and mint drain receive significant quantities of groundwater because the entire study site is located in the floodplain of the Wisconsin River where the surface aquifer is near the ground surface. Relatively free of elemental contamination, this groundwater contributes to the dilution of the ash effluent. The ash effluent is also diluted by water from the mint drain and Rocky Run Creek. The mint drain is a channelized stream about 3.5 km long that drains an area of 7.8 km^2 composed primarily of mint fields and wetlands. Rocky Run Creek is an ungauged watercourse draining an area approximately 65 km^2 that consists primarily of farmland, woods, and wetlands. The creek extends about 20 km from its source at Mud Lake (in central Columbia County) to its confluence with the Wisconsin River. The junction of the ash drain with

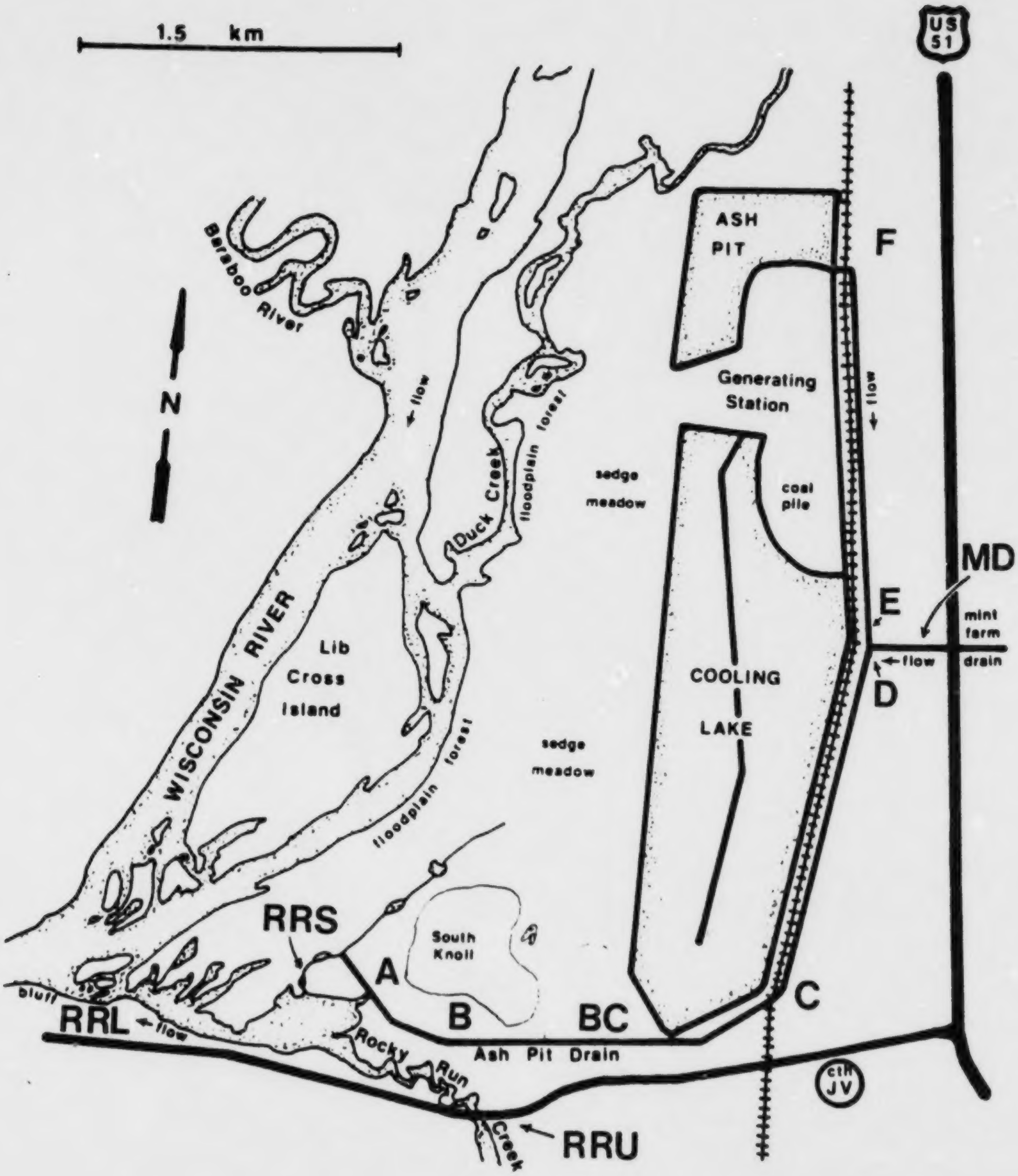

Figure 3. Sampling sites for the collection of aquatic organisms.

Rocky Run Creek is about 800 m upstream from the Wisconsin River. The volume of water flow in Rocky Run Creek is considerably greater than that of the ash drain.

The ashpit must be drained by pumping when it is filled by ground water, precipitation, and water added in the slurry of fly ash and bottom ash. The effluent is carried away by the ashpit drain. Pumping began on 24 April 1975. A pump log is maintained by the WPL. The usual practice has been to pump on a 12-h daily schedule. During periods of little precipitation, little or no effluent is discharged from the ashpit for several weeks at a time. This results in periods of no flow in the stretch of the ashpit drain above the confluence with the mint drain. In view of the situation, the sampling site closest to the ashpit (site D) was established just downstream from the confluence of the mint drain and the ashpit drain. Samples also were taken from the mint drain for use as controls. Sampling sites C, BC, B, and A were set up 2.1, 2.9, 3.4, and 4.0 km downstream from site D. About 250 m downstream from site A, the ashpit drain joins a slough of Rocky Run Creek.

The substrata of the mint drain and the ashpit drain are predominantly silt. Patches consisting of organic debris and a few rocks (5 to 30 cm in diameter) are scattered throughout the mint drain and the ash drain. These patches provide significant habitat for aquatic organisms. Silt substrates predominate at the RRU site as well; however, significant additional habitat is provided by emergent vegetation and organic debris. The substrate at the RRL site (south bank) is composed of silt and sand. Macrophytes (e.g., *Potamogon* sp. and *Ceratophyllum* sp.) were plentiful at the times when most samples were obtained.

The pH of the ashpit effluent ranges from 10 to 12 because of the hydrolysis reactions of the oxides of the alkali and alkaline earth elements in the fly ash. The pH of the ashpit effluent is reduced to pH 7 to 9 before it joins the mint drain by adding H_2SO_4. The acid is added just after the effluent leaves the discharge pipe. The pH of the mint drain and Rocky Run Creek varies from 7.1 to 8.2 during the year.

Sampling and Preparation

Taxonomic information for the invertebrate organisms studied are given in Table 2. Samples were collected from 1974 through 1978 at the sites shown in Figure 3. Most organisms were collected with a nylon dip net. The only metal part of the dip net was a brass bracket joining the net to an extension pole; no organisms came into contact with the brass. To collect organisms, the dip net was dragged through sections of the bottom that seemed likely to provide good habitat for benthic invertebrates. The contents of the dip net were dumped on the stream bank. Specimens were removed from the sediments with stainless steel forceps and placed in plastic or glass vials or plastic bags. Water from the collection was added to the sample containers.

Artificial substrate samplers also were used to collect organisms. The samplers consisted of nylon-mesh produce bags containing limestone rock fragments 3 to 7 cm in diameter. The samplers were allowed to rest gently in the stream bottom. Air-filled plastic jugs were used as floats to prevent the samplers from sinking where the sediments were soft. Nylon dish-scouring pads tied to the hemp or nylon twine that connected the floats to the stone samplers served as additional artifical substrates. The substrates usually were colonized by organisms within 4 weeks. At the time of collection the rock substrates were removed from the water and placed in a plastic tub. The net was slashed to free the rocks for examination.

TABLE 2. TAXONOMIC INFORMATION FOR THE INVERTEBRATE ORGANISMS ANALYZED

Class	Subclass	Order	Family	Genus and species
Crustacea	Malacostraca	Amphipoda	Gamaridae	*Gammarus*
			Talitridae	*Hyallela azteca*
		Isopoda	Asellidae	*Asellus racovitzai*
Insecta		Coleoptera	Gyrinidae	*Dineutus*
		Hemiptera	Corixidae	*Hesperocorixa* *Sigara*
		Odonata	Aeshnidae	*Anax*
			Corduliidae	*Tetragoneuria*
			Libellulidae	*Libellula* *Sympetrium*

Specimens were captured and stored as previously described. The nylon dish scouring pads were placed directly into plastic bags containing site water and examined for organisms in the laboratory. All samples were stored in an ice-filled cooler until they were prepared for laboratory analysis.

Prior to analysis, all organisms were washed in the laboratory by allowing the organisms to move about in containers of distilled-deionized water. Three successive baths lasting about 5 min each were normally used. The washed specimens were blotted dry with paper toweling, counted and placed in clean, pre-weighed vials. The vials were weighed to obtain estimates of the wet ("fresh") weight and the samples were stored in a freezer. Most of the organisms remained alive until the time of freezing. Prior to analysis, the frozen samples were lypholized to constant mass in a pyrex freeze dryer with liquid N and dry ice cold traps.

In order to estimate the effects of ingested material on the measured concentrations of elements in the samples of organisms, samples of *Asellus racovitzai* were held in baths of distilled-deionized water at 8 to 10°C for up to 1 week to allow the organisms to empty their guts. The water was changed daily. The material eliminated by the organisms was collected by filtering and dried at 60°C in preparation for analysis. Ingested material was easily visible in the organisms when they were examined in bright light. Specimens with empty guts were removed, washed, weighed, and frozen on a daily basis.

Several samples of frogs (*Rana pipiens*) also were collected in the ashpit drain on 8 November 1974 and 13 August 1975 and analyzed to determine if any elements had accumulated by organisms higher in the food chain. The frog specimens were dissected with stainless steel scalpels, forceps and scissors on either glass or stainless steel trays. Utensils used to remove the organs were cleaned immediately before the operation and not used again before washing. All glassware and instruments were washed with "Micro" brand detergent, and rinsed in distilled-deionized water, ethanol and again in distilled-deionized water. Organs were removed whole by carefully cutting blood vessels and connective tissue and lifting them out with forceps. Skin samples were obtained by peeling off centimeter-size pieces. All samples were placed in preweighed glass vials and after "fresh" weights were obtained stored in the freezer. After freeze drying, composite samples of muscle tissue were made by cutting the tissue with stainless steel scissors and grinding it in an agate mortar until a fine, easily poured powder was obtained. Equal masses of tissue from each specimen were used to make the composite sample. The lypholized liver tissues were not ground prior to the preparation of composite samples. To ensure that the contribution of each specimen to the whole composite sample was similar for all specimens, large pieces of liver were trimmed to size with a pair of surgical scissors.

Analytical Procedures

Elemental concentrations in the samples were determined by nondestructive neutron activation analysis (Koons and Helmke 1978). Radiochemical separations after neutron irradiation were performed to determine Cd, Cu, and Hg using modifications of the techniques of Henzler et al. (1974).

For nondestructive neutron activation, the standards and freeze-dried samples, which usually weighed between 30 and 150 mg each, were placed in pre-weighed, high purity quartz tubing that was heat sealed at one end. The sample and tubing were reweighed, and the tube was heat sealed. Samples of U.S. Geological Survey SCo-1 (Cody Shale) and National Bureau of Standards SRM 1577 (Bovine Liver) were used as standards. The samples and standards were irradiated in the University of Wisconsin Nuclear Reactor at a neutron flux of approximately 9.9×10^{12} neutrons/cm^2/sec for 6 h. Iron wire flux monitors wrapped around each tube were used to compare the neutron flux received by each standard with the flux received by each sample. Flux corrections were calculated by comparing the specific γ-ray activity for standard and sample iron wire monitors. Following activation, samples and standards were quantitatively transferred from the tubes and sealed in polyethylene pouches of 1 cm diameter. The samples and standards were radioassayed 0, 3, 10, and 40 days after irradiation (Denechaud et al. 1970, Henzler et al. 1974, Koons and Helmke 1978).

OAK LEAVES

The small percentage of fly ash that escapes the electrostatic precipitators of modern coal-fired generating stations is dispersed widely in the environment. This fly ash, together with other anthropogenic dusts, mixes with natural dusts (such as dust from soil) to form the aerosolic dust that is continuously removed from the atmosphere by various processes. A portion of this aerosolic dust is deposited on vegetation by wet and dry fallout or by impaction. Elements from the particles of fly ash, especially elements present in high concentrations on the surfaces of the fly ash particles (Natusch et al. 1974), presumably can dissolve on leaf surfaces where they are available for plant uptake or where they may provoke injurious reactions. Oak (*Quercus* spp.) leaves were studied to determine if this occurs. Oak leaves were selected because they are common in the region and because oak trees have deep and extensive root systems which should minimize seasonal variations in the concentrations of trace elements due to variations in element uptake from the soil.

The effects of a single generating station are likely to be so small that they cannot be measured since the tall stacks used with modern stations disperse the fly ash over large areas so that little or no fly ash is concentrated within several km of the station. Exceptions to this general pattern can occur when unusual wind conditions cause the plume from the stack to touch down. Intense fumigation of small areas can then occur. They are usually transitory events. The sample sites were selected to be within 12 km of the stack because fly ash from the Columbia Generating Station would be unmeasurably diluted at greater distances. Any indication of the effect of the Columbia Generating Station must depend on the chance sampling of an area that has been fumigated by the plume. Since the effect of fly ash is regional and the effect of a single generating station is difficult to measure, the sampling limitation is not a serious disadvantage.

The major objectives were: (1) To gather accurate and precise data for oak leaves to provide a reliable baseline for future studies, and (2) to determine the effect, if any, of fly ash from the Columbia Generating Station.

In relation to the first objective, a study was conducted to determine what fraction of the total concentration of each element in the sample is present as inorganic contamination, mainly dust. Since some elements are present at relatively high concentrations in inorganic material but are present at low concentrations in samples of biological tissue, an effective procedure for washing oak leaves was determined. Electron microscopy with x-ray fluorescence was used to determine the types of inorganic particles on the leaf surfaces. Elements such as the rare earths and Sc, Ga, and Hf that are only slightly accumulated by leaves but occur at relatively high concentrations in inorganic dusts, can be used to indicate the extent of inorganic contamination.

Samples of oak leaves (white oak, *Quercus alba*; black oak, *Q. velutina*; and red oak, *Q. rubra*) were collected at sites located 0.1 to 12 km from the Columbia Generating Station. The sampling sites are shown in Figure 4.

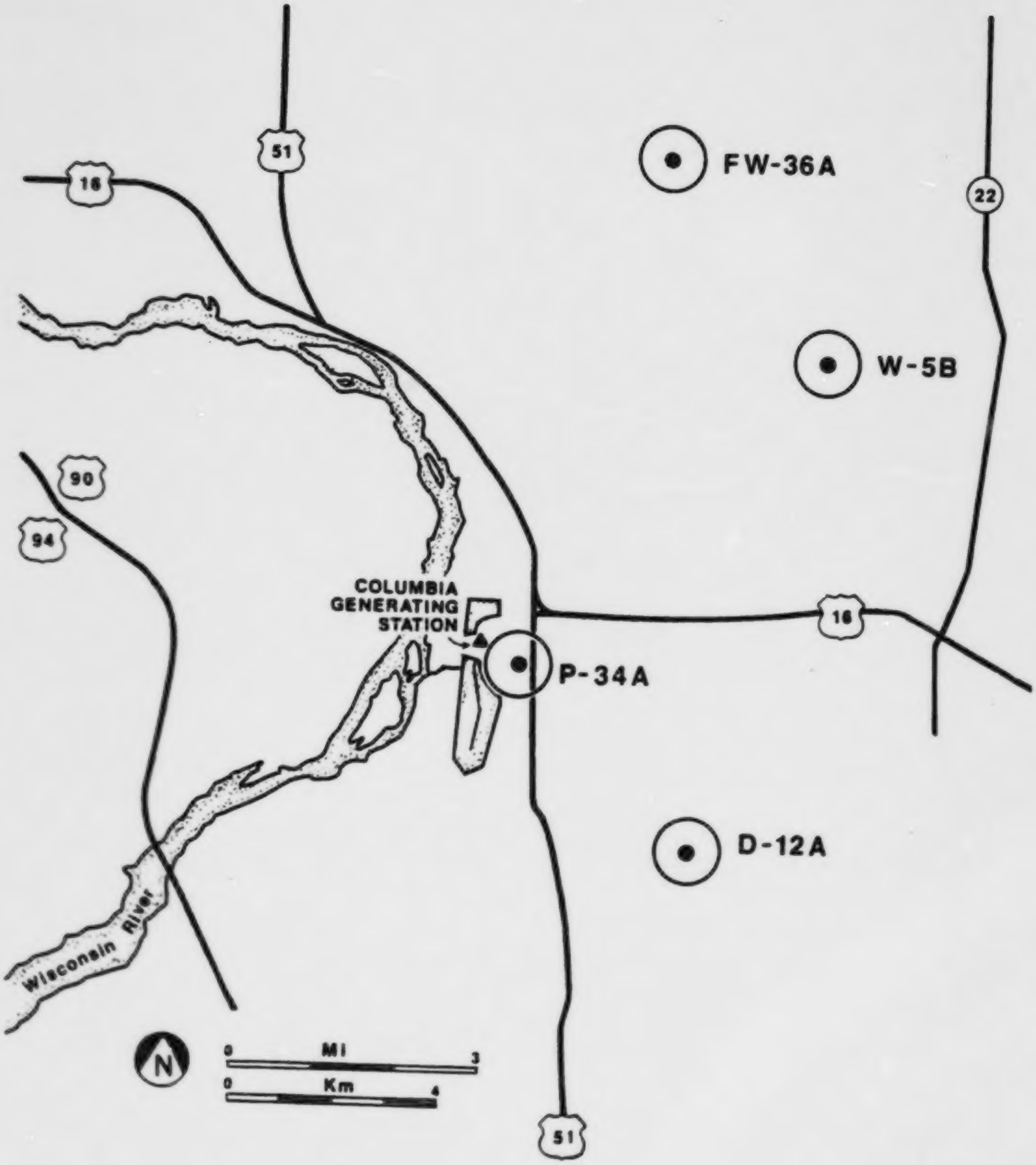

Figure 4. Locations of smapling sites for oak leaves.

Since there are prevailing westerly winds in this region, the sites were selected east of the power plant. The sites are located on small hills in oak woods. The black oak family includes hybrids between black oak and red oak; no attempt was made to distinguish between them. The oak leaf samples were collected from mature trees. The same trees were sampled on each collection date. Only leaves < 2.5 m (8 ft) from the ground were collected. Leaves were selected to be free from visible insect damage or disease. The collectors wore polyethylene gloves and the samples were put into polyethylene bags. As many individual trees as possible were sampled to obtain 20 to 60 leaves from each species at each site. Samples were collected at four intervals during each growing season.

Most of the samples of black oak were not washed so that electron microscopy could be performed to determine the abundance of the aerosolic dust on the leaf surfaces.

Effects of Washing the Leaves

To evaluate the effects of washing on the concentrations of elements in oak leaves, 60 fresh leaves from a single white oak were divided randomly into three groups. The first group was not washed, the second group was washed three times (30 sec each) with distilled water, and the third group was washed once with 0.1 *M* HCl and twice with distilled water. The leaves were washed by placing them in a plastic bag with about 500 ml of water and then shaking the bag while holding the top closed. The samples were air-dried, dried at 40°C and ground to pass a 40-mesh sieve.

To estimate the sampling error, 15 replicate samples, each containing 25 white oak leaves, and a similar set of samples of black oak leaves were collected from sites D12 and FW36 on 9 September 1976. The leaves were washed three times with water and handled in the normal manner.

Bioaccumulation of Elements in Leaves

To determine the bioaccumulation of elements used as indicators of inorganic contamination, oak trees were grown from acorns in a sandy loam soil from sampling site D12 that was treated with radiotracers of Eu, Tb, Hf, and Sc. The leaves were harvested and radioassayed to determine the uptake of each tracer.

To prepare the radiotracers, a solution containing 5.0 mg each of Eu, Sc, and Tb and 6.5 mg of Hf as their nitrates was weighed into four quartz tubes. The solutions were evaporated to dryness and the tubes heat sealed. The samples were irradiated for 6 h at a neutron flux of 5×10^{12} neutrons/cm^2/sec. The tubes were opened 14 days later. Their contents were dissolved in 2.0 ml of concentrated HNO_3 and rinsed into a 250-ml volumetric flask. After dilution to volume, 1 ml was removed and preserved to serve as a standard for the radioassays. Four piles of soil, each weighing 3.90 kg, were formed on large plastic sheets and the tracer solutions were mixed with the soil. This was done by spreading soil about 1 cm thick, adding the solution dropwise, mixing, and repeating the process as necessary. Each pile of soil contained 5 mg of irradiated Eu, Sc, and Tb and 6.5 mg of Hf.

Afterwards, the soil-tracer system was allowed to equilibrate through a wet-dry-wet-dry cycle for 3 days, the soils were placed into four pots lined with plastic bags. Three sprouted acorns (*Q. alba*) previously treated with a temperature cycle to encourage sprouting were planted in each pot.

Seedlings emerged within a few weeks. They were grown for 10 months in a greenhouse until each had eight or more leaves. All except the lowest four leaves from each seedling were harvested, dried, placed in vials, and radioassayed using a lithium-drifted germanium [Ge(Li)] detector and a multichannel analyzer. An aliquot of the standard also was assayed. The isotopes and γ-ray energies used were the same as those used for the 40-day assay for neutron activation analysis (Koons and Helmke 1978). The elemental concentrations in the leaves were calculated from the radioassay results.

Analytical Procedures

The samples were analyzed by nondestructive and radiochemical neutron activation (Koons and Helmke 1978, Henzler et al. 1974). The samples were irradiated in the University of Wisconsin Nuclear Reactor. The -ray radioassays were done in the Department of Soil Science using one of three Ge(Li) detectors (Ortec or Canberra) coupled to a computer-based multichannel analyzer (Tracor Northern model TN-11). Sulfur and P were determined by crystal dispersive x-ray fluorescence analysis (Rigoku model 2064) in the Department of Soil Science. For electron microscopy, portions of the leaves were mounted on Al stubs and coated with Au-Pd. The analyses were conducted in the Department of Geology on a JEOL Model JSM-50A instrument.

SECTION 4

RESULTS

COAL

The results of the coal analyses are given in Tables 3 through 5. The analytical uncertainties associated with the concentration of each element is given in the first column of Table 3. The concentrations of most elements are lower in western coals than in the three samples from Illinois. Exceptions are the concentrations of Ba, Ca, Hf, Mn, Ta, and Th. Few elements are thought to have significant concentrations associated with the C in the coal. Instead, most of each element in coal results from the presence of the silicate or other inorganic components. The amount of inorganic material and its composition can differ for each deposit.

The high concentration of Ca in Wyoming and Montana coals results from their high content of calcite ($CaCO_3$). Calcite usually has low concentrations of other elements, except Mg, Sr, and Ba, which partially accounts for the low concentrations of elements in these coals. In contrast, the Illinois coals have relatively high concentrations of clays and Fe oxides. Both of these inorganic components have high concentrations of many elements. Based on these analyses, it is expected that the fly ash from Wyoming and Montana coals having high concentrations of lime, will be basic while fly ash from Illinois coals, with high concentrations of Fe will be acidic.

FLY ASH

The concentration of elements in the samples of fly ash from the Colstrip, Mont., and Belle Ayr, Wyo., coals are given in Tables 6 through 11. The analytical uncertainty expressed as the percent one standard deviation given in Table 3 also applies to the data in these tables. In general, the concentrations of almost all elements in fly ash are greater in the third stage than in the first. Exceptions are Fe, which decreases, and Hf, K, and Se, which have about the same concentrations in all stages. Arsenic and Sb show the greatest increase in concentration; by a factor of about three. The fractionation of the elements is thought to result from various factors, including particle size, resistivity of the particles, and condensation of volatile species (Davison et al. 1974, Natusch et al. 1974). The general trend is that most transition elements occur at the highest concentrations in the particles of smallest size.

Elements that are volatile at the temperature of the flame in the boiler tend to be concentrated in fly ash from the last stages of the

TABLE 3. ELEMENTAL ANALYSIS (μg/g) OF FOUR SAMPLES OF COAL USED IN 1974

Element	Coal used by power plants			
(S.D., %)[a]	Edgewater	Nelson Dewey	Rock River	Colstrip
As (10)	10	3.6	66	1.0
Ba (4)	< 60	< 30	< 50	280
Ca (10)	---	---	---	---
Cd (15)	< 0.25	0.26	0.51	0.22
Ce (1)	5.6	7.1	13.6	5.6
Co (3)	5.0	2.9	4.8	0.41
Cr (5)	48	46	42	9
Cs (10)	---	---	---	---
Cu (5)	12	9.2	14	8.3
Eu (1)	0.17	0.22	0.36	0.16
Fe (1)	10,000	12,000	22,000	---
Ga (10)	---	3.7	6.2	4.7
Hf (5)	0.62	0.62	0.69	1.9
Hg (10)	0.13	0.070	0.18	0.042
K (15)	---	---	---	---
La (3)	4.2	4.3	9.6	3.8
Lu (3)	0.10	0.12	0.13	0.099
Mn (1)	25	32	24	87
Na (1)	310	310	640	150
Nd (15)	---	---	---	---
Rb (15)	29	28	45	< 5
Sb (5)	2.4	0.36	1.8	0.41
Sc (1)	3.3	2.6	3.4	1.5
Se (10)	2.4	2.4	2.4	0.75
Sm (2)	0.86	1.2	1.9	0.71
Ta (20)	0.17	0.19	0.39	0.51
Tb (3)	0.20	0.22	0.29	0.27
Th (5)	2.0	2.0	2.5	3.8
U (10)	---	---	---	---
Yb (3)	---	---	---	---
Zn (5)	29	42	110	7.6

[a] S.D. is percent for one standard deviation based on counting statistics.

TABLE 4. ELEMENTAL ANALYSIS (μg/g) OF FOUR SAMPLES OF COAL FROM COLSTRIP USED AT THE COLUMBIA I PLANT IN 1975

Element (S.D., %)[a]	#76 5/3/75	#80 5/13/75	#85 5/26/75	#86 5/27/75
As (10)	0.72	1.0	1.1	1.0
Ba (4)	610	590	700	660
Ca (10)	10,000	13,000	11,000	12,000
Cd (15)	---	---	---	---
Ce (1)	4.2	6.9	7.2	6.7
Co (3)	0.31	0.54	0.53	0.47
Cr (5)	2.5	4.4	4.5	4.0
Cs (10)	0.08	0.09	0.17	0.14
Cu (5)	7.0	7.0	6.9	6.9
Eu (1)	0.059	0.092	0.11	0.090
Fe (1)	1,600	2,700	3,400	2,700
Ga (10)	---	---	---	---
Hf (5)	0.49	0.84	0.85	0.84
Hg (10)	0.020	0.042	0.031	0.027
K (15)	190	190	260	270
La (3)	2.5	4.1	4.3	3.8
Lu (3)	0.030	0.051	0.043	0.048
Mn (1)	72	120	140	130
Na (1)	120	180	230	150
Nd (15)	1.7	4.0	3.1	---
Rb (15)	0.90	---	2.0	---
Sb (5)	0.53	0.81	0.88	0.81
Sc (1)	0.66	1.1	1.1	1.1
Se (10)	0.06	0.10	0.09	---
Sm (2)	0.35	0.56	0.61	0.57
Ta (20)	---	---	---	---
Tb (3)	0.023	0.12	0.13	0.12
Th (5)	1.4	2.5	2.5	2.5
U (10)	0.35	0.61	0.67	0.61
Yb (3)	0.17	0.25	0.28	0.27
Zn (5)	3.3	5.4	5.5	5.4

[a] S.D. is percent for one standard deviation based on counting statistics.

TABLE 5. ELEMENTAL ANALYSIS (μg/g) OF COAL FROM BELLE AYR, WYOMING USED AT THE COLUMBIA I PLANT IN 1978

Element (S.D., %)[a]	Amax	Tripper	Composite
As (10)	---	---	---
Ba (4)	96	440	120
Ca (10)	18,000	16,000	20,000
Cd (15)	---	---	---
Ce (1)	7.6	6.4	6.1
Co (3)	1.1	0.76	0.57
Cr (5)	2.8	3.4	3.7
Cs (10)	---	---	0.39
Cu (5)	---	---	---
Eu (1)	0.15	0.097	0.13
Fe (1)	6,700	2,700	3,800
Ga (10)	---	---	---
Hf (5)	0.40	0.41	0.39
Hg (10)	---	---	---
K (15)	---	---	---
La (3)	4.8	4.2	3.7
Lu (3)	0.012	0.0007	0.0088
Mn (1)	---	---	---
Na (1)	66	200	170
Nd (15)	---	---	---
Rb (15)	---	---	---
Sb (5)	1.7	1.4	2.2
Sc (1)	1.3	1.2	1.5
Se (10)	0.80	1.4	0.90
Sm (2)	0.59	0.56	0.56
Ta (20)	---	---	0.13
Tb (3)	0.059	0.046	0.22
Th (5)	2.3	2.2	2.7
U (10)	---	---	---
Yb (3)	0.32	0.20	0.23
Zn (5)	---	1.2	2.0

[a] S.D. is percent for one standard deviation based on counting statistics.

TABLE 6. ELEMENTAL COMPOSITION (μg/g) OF FLY ASH AS DETERMINED BY NEUTRON ACTIVATION ANALYSIS; 5 SEPTEMBER 1975

Element (S.D., %)[a]	Stage 1	Stage 2	Stage 3	Bottom slag
As (10)	8.0	21	24	1.7
Ba (4)	7,200	8,200	10,000	4,500
Ca (10)	91,000	120,000	130,000	94,000
Cd (15)	0.90	1.6	1.5	---
Ce (1)	70	96	99	59
Co (3)	7.8	11	11	6.6
Cr (5)	38	64	68	36
Cs (10)	1.2	1.5	1.4	0.87
Cu (5)	60	90	100	---
Eu (1)	0.97	1.3	1.4	1.1
Fe (1)	69,000	34,000	28,000	9,400
Ga (10)	24	52	61	---
Hf (5)	8.8	8.6	8.8	10
Hg (10)	< 0.002	< 0.002	< 0.003	---
K (15)	3500	4,400	3,600	3,100
La (3)	37	52	54	35
Lu (3)	0.48	0.62	0.64	0.46
Mn (1)	860	1,100	1,100	---
Na (1)	1,900	2,400	2,400	2,200
Nd (15)	29	40	42	30
Rb (15)	16	24	18	---
Sb (5)	4.2	9.1	11	1.5
Sc (1)	9.8	14	14	8.9
Se (10)	2.8	2.6	3.1	2.2
Sm (2)	5.7	8.1	8.5	5.2
Ta (20)	---	---	---	---
Tb (3)	1.2	1.6	1.6	0.77
Th (5)	22	29	30	21
U (10)	7.0	10	12	3.5
Yb (3)	2.9	3.5	3.4	3.1
Zn (5)	50	79	83	---

[a] S.D. is percent for one standard deviation based on counting statistics.

TABLE 7. ELEMENTAL COMPOSITION (μg/g) OF FLY ASH AS DETERMINED BY NEUTRON ACTIVATION ANALYSIS; 22 APRIL 1976

Element (S.D., %)[a]	Columbia I Fly Ash		
	Stage 1	Stage 2	Stage 3
As (10)	16	22	22
Ba (4)	6,400	8,100	9,000
Ca (10)	150,000	160,000	160,000
Cd (15)	---	---	---
Ce (1)	90	99	100
Co (3)	9.7	11	11
Cr (5)	61	71	73
Cs (10)	1.8	2.3	2.2
Cu (5)	---	---	---
Eu (1)	1.3	1.5	1.5
Fe (1)	40,000	36,000	34,000
Ga (10)	---	---	---
Hf (5)	8.9	8.5	8.9
Hg (10)	---	---	---
K (15)	4,200	4,800	4,900
La (3)	52	58	60
Lu (3)	0.58	0.65	0.70
Mn (1)	---	---	---
Na (1)	2,200	2,100	2,000
Nd (15)	39	46	51
Rb (15)	25	38	33
Sb (5)	7.7	10	11
Sc (1)	13	15	15
Se (10)	3.5	3.4	3.1
Sm (2)	7.7	8.7	8.8
Ta (20)	---	---	---
Tb (3)	1.0	1.2	1.2
Th (5)	28	30	31
U (10)	9.0	9.0	11
Yb (3)	3.7	3.8	3.9
Zn (5)	---	---	100

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[a] S.D. is percent for one standard deviation based on counting statistics.

TABLE 8. ELEMENTAL COMPOSITION (μg/g) OF FLY ASH AS DETERMINED BY NEUTRON ACTIVATION ANALYSIS; 7 FEBRUARY 1978

Element (S.D., %)[a]	Columbia Fly Ash Stage 1	Columbia Fly Ash Stage 2	Columbia Fly Ash Stage 3
As (10)	18	33	38
Ba (4)	4,000	4,200	5,800
Ca (10)	190,000	190,000	220,000
Cd (15)	---	---	---
Ce (1)	70	79	89
Co (3)	8.7	11	12
Cr (5)	38	48	50
Cs (10)	4.6	4.7	5.4
Cu (5)	---	---	---
Eu (1)	1.1	1.2	1.8
Fe (1)	69,000	45,000	39,000
Ga (10)	---	---	---
Hf (5)	4.9	5.0	4.9
Hg (10)	---	---	---
K (15)	---	---	---
La (3)	44	48	56
Lu (3)	0.47	0.11	0.50
Mn (1)	---	---	---
Na (1)	38,000	36,000	29,000
Nd (15)	31	35	36
Rb (15)	31	38	31
Sb (5)	19	28	35
Sc (1)	15	16	19
Se (10)	6.8	9.5	7.6
Sm (2)	6.3	6.9	7.8
Ta (20)	1.5	1.7	1.7
Tb (3)	0.74	0.83	0.92
Th (5)	29	31	35
U (10)	---	---	---
Yb (3)	2.6	2.7	2.8
Zn (5)	---	---	---

[a] S.D. is percent for one standard deviation based on counting statistics.

TABLE 9. ELEMENTAL COMPOSITION (μg/g) OF FLY ASH AS DETERMINED BY NEUTRON ACTIVATION ANALYSIS; 8 MARCH 1978

Element	Columbia I Fly Ash		
(S.D., %)[a]	Stage 1	Stage 2	Stage 3
As (10)	23	31	42
Ba (4)	3,800	3,700	6,300
Ca (10)	210,000	230,000	230,000
Cd (15)	---	---	---
Ce (1)	76	92	100
Co (3)	12	13	17
Cr (5)	42	50	62
Cs (10)	4.7	5.8	6.2
Cu (5)	---	---	---
Eu (1)	1.2	1.5	1.5
Fe (1)	72,000	47,000	40,000
Ga (10)	---	---	---
Hf (5)	5.4	5.5	5.3
Hg (10)	---	---	---
K (15)	---	7,100	---
La (3)	46	57	60
Lu (3)	0.11	0.56	0.13
Mn (1)	---	---	---
Na (1)	17,000	11,000	16,000
Nd (15)	39	37	48
Rb (15)	---	45	---
Sb (5)	22	31	44
Sc (1)	16	19	21
Se (10)	4.3	2.6	3.3
Sm (2)	6.9	8.0	8.9
Ta (20)	1.7	1.8	2.1
Tb (3)	0.82	0.97	1.0
Th (5)	30	35	38
U (10)	---	---	---
Yb (3)	3.0	3.5	3.5
Zn (5)	---	---	---

[a] S.D. is percent for one standard deviation based on counting statistics.

TABLE 10. ELEMENTAL COMPOSITION (μg/g) OF FLY ASH AND STACK SAMPLES AS DETERMINED BY NEUTRON ACTIVATION ANALYSIS; 9 JULY 1976

Element (S.D., %)[a]	Columbia I fly ash	Columbia I stack samples		
As (10)	27	20	17	8.0
Ba (4)	3,800	9,100	8,400	3,800
Ca (10)	320,000	140,000	180,000	84,000
Cd (15)	---	---	---	---
Ce (1)	140	100	98	65
Co (3)	25	12	11	6.3
Cr (5)	82	76	72	82
Cs (10)	11	1.7	1.4	1.1
Cu (5)	---	---	---	---
Eu (1)	3.1	1.3	1.3	0.86
Fe (1)	50,000	32,000	40,000	38,000
Ga (10)	---	---	---	---
Hf (5)	5.8	9.1	8.6	6.6
Hg (10)	---	---	---	---
K (15)	5,300	3,500	3,600	25,000
La (3)	81	59	54	37
Lu (3)	0.80	0.62	0.60	0.40
Mn (1)	---	---	---	---
Na (1)	7,000	2,900	2,700	3,400
Nd (15)	71	46	50	29
Rb (15)	68	20	20	16
Sb (5)	13	11	9.0	4.3
Sc (1)	35	15	14	8.9
Se (10)	3.6	14	710	18
Sm (2)	13	8.5	7.9	5.3
Ta (20)	2.0	---	---	---
Tb (3)	1.8	1.1	1.1	0.70
Th (5)	40	32	30	20
U (10)	---	6.0	5.0	3.0
Yb (3)	5.3	4.6	4.2	2.8
Zn (5)	---	110	100	69

[a] S.D. is percent for one standard deviation based on counting statistics.

TABLE 11. ELEMENTAL COMPOSITION (μg/g) OF STACK SAMPLES AS DETERMINED BY NEUTRON ACTIVATION ANALYSIS; 14 JULY 1976

Element (S.D., %)[a]	Columbia I stack samples			
As (10)	15	22	10	17
Ba (4)	7,300	9,400	4,700	4,700
Ca (10)	140,000	150,000	120,000	120,000
Cd (15)	---	---	---	---
Ce (1)	88	110	74	95
Co (3)	10	13	8.1	12
Cr (5)	57	75	130	220
Cs (10)	1.5	1.6	1.2	1.6
Cu (5)	---	---	---	---
Eu (1)	1.2	1.4	1.0	1.2
Fe (1)	45,000	31,000	62,000	31,000
Ga (10)	---	---	---	---
Hf (5)	8.2	8.7	8.7	8.5
Hg (10)	---	---	---	---
K (15)	3,800	3,900	3,100	3,300
La (3)	49	61	42	55
Lu (3)	0.55	0.64	0.51	0.61
Mn (1)	---	---	---	---
Na (1)	2,500	2,900	3,400	4,600
Nd (15)	37	45	34	41
Rb (15)	28	21	16	27
Sb (5)	7.9	12	4.9	9.3
Sc (1)	12	15	10	14
Se (10)	14	10	28	23
Sm (2)	7.4	9.0	6.3	8.1
Ta (20)	---	---	---	---
Tb (3)	1.0	1.1	0.84	0.93
Th (5)	27	37	24	29
U (10)	5.0	7.0	5.0	6.0
Yb (3)	3.3	3.8	3.4	4.5
Zn (5)	90	130	71	85

[a] S.D. is percent for one standard deviation based on counting statistics.

precipitator. This occurs because the volatile elements condense on the surfaces of the fly ash particles as heat is extracted from the flue gas. The smaller particles which have a higher ratio of surface area to volume than do larger particles, are more concentrated in the last stages of the precipitator, resulting in the highest concentrations of volatile elements. The surface enrichment of the volatile elements, many of which are potentially toxic, is a major concern in terms of the environmental and health impact of fly ash.

The concentrations of Ca and Ba in these fly ashes are among the highest reported. Mercury is present in uniformly low concentrations in all samples analyzed. The concentrations of Se are greater than those found in most soils but they are low enough so that no toxicity problems will occur if this fly ash is used on agricultural soils. The concentrations of B were analyzed in only a few samples. Its concentration ranged from 500 to 800 µg/g. These concentrations could induce severe B toxicity symptoms in plants if large amounts of fly ash were spread on relatively small areas. The concentrations of Pb and Be, measured in only a few samples, were about 6 and 0.04 µg/g, respectively. The concentrations of B, Ba, Ca, Na, Sb, and Se are significantly higher in the fly ashes than in most soils. However, only B poses serious concern for the utilization of fly ash as a soil amendment.

Distribution of Particle Sizes

Fly ash samples collected in September 1975 and April 1976 were studied intensively because WPL and the manufacturer of the precipitators were having difficulty achieving the design rating for fly ash removal.

The efficiency of the precipitators in trapping particles is determined mainly by the composition of the ash and the temperature of the gases carrying the ash as it passes through the precipitator. The composition of the ash affects its electrical properties and therefore the efficiency of collection. The electrical property most useful in predicting the collection efficiency is surface resistivity, which is low temperature, surface electrical resistance. Bickelhaupt (1975) observed that the surface resistivity of ash particles is inversely proportional to the concentrations of the alkaline metals in the ash and, even more so, on its surface. This factor is most notable for Na. When values of resistivity versus temperature of the particles are plotted, the resultant figure is an inverted V with a maximum resistivity in the area of 182°C. A typical illustration of this can be seen in Figure 5. The low temperature part of the curve is due mainly to surface resistivity of the particles whereas the upper temperature portion is due mainly to volume resistivity. Of the two ashes plotted in Figure 5, the curve with the higher resistivity contains 0.25% Na_2O and that with the lower has 2.31%. It has been demonstrated by Bickelhaupt (1975) that volume resistivity is dependent on an ionic conducting mechanism in which Na^+ is the principal charge carrier.

In a study of six types of electrostatic precipitators, McCain et al. (1975) found that minimum collection efficiency occurred in the particle size range 0.1 to 0.5 µm. The results suggest that collection efficiency is

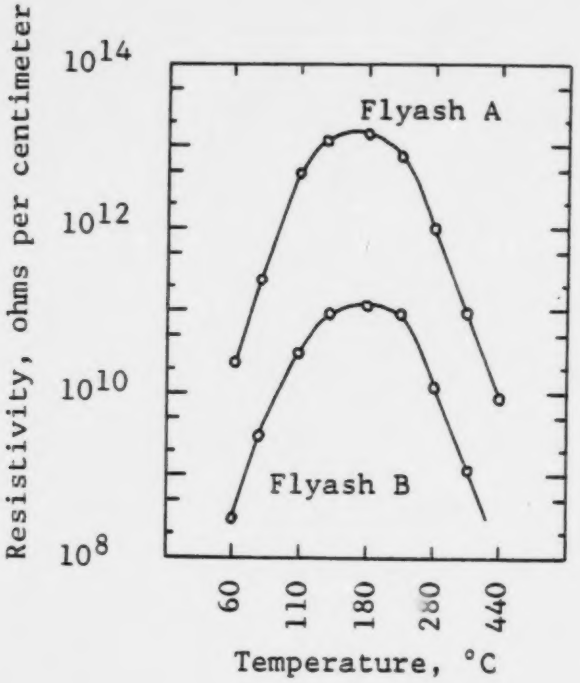

Figure 5. Resistivity of two fly ashes as a function of temperature. Sodium oxide content of fly ashes A and B are 0.25 and 2.3% respectively (after Bickelhaupt, 1975).

high for particles above and below that range, which is significant in terms of the potential hazard that particles < 0.1 µm pose to mammalian respiratory systems. Electrostatic precipitators were designed originally for power stations burning Fe-rich eastern coals. The Fe is considered important for two reasons: It increases the surface resistance of fly ash, thus making precipitators more efficient, and it is necessary for bonding S to the ash. A Na_2CO_3-based conditioner was added to the coal in 1975 to improve the efficiency of the precipitator. In 1977, the conditioner was changed to one based on $(NH_4)_2SO_4$, which is still being used. The precipitator is now operating at its design rating of 99.5% efficiency.

Figure 6 is a photocomposite of the material collected from stages I through III in September 1975. This figure shows a wide variety of particle sizes in each of the precipitator stages, with a distinct decrease in mean grain size from stages I through III. The particles generally are spherical and round[1] and quite simple in appearance. There are a few particles, however, with irregular shapes, especially in samples from the first precipitator stage; these samples also contain a number of composite particles (i.e., large grains with smaller ones attached to them).

The distribution of particle sizes in the samples presented in Figure 7, shows a decrease in the mean diameter from 4.49 µm in stage I to 2.08 µm in stage III. A high standard deviation is associated with these means for two reasons: 1) There is a long-tailed distribution of the population in the coarse region and 2) the population studied is strongly truncated for the smallest particles.

The materials collected in April 1976 show a similar morphology to those collected in September 1975. They exhibit a wide range in particle size, but the range is smaller than that of the September samples. The distribution of sizes measured for this set of samples is shown in Figure 8, along with the mean diameter and standard deviation for each stage.

The third set of samples analyzed for this study was collected in July 1976. The WPL, in an attempt to identify its problems with respect to precipitator performance, conducted tests at full power at that time. Test samples were collected from ports between the outlets of the precipitators and the base of the stack; samples collected from the north and south precipitator outlets during two of these tests were made available for analysis in the present study. The materials were collected in alundum

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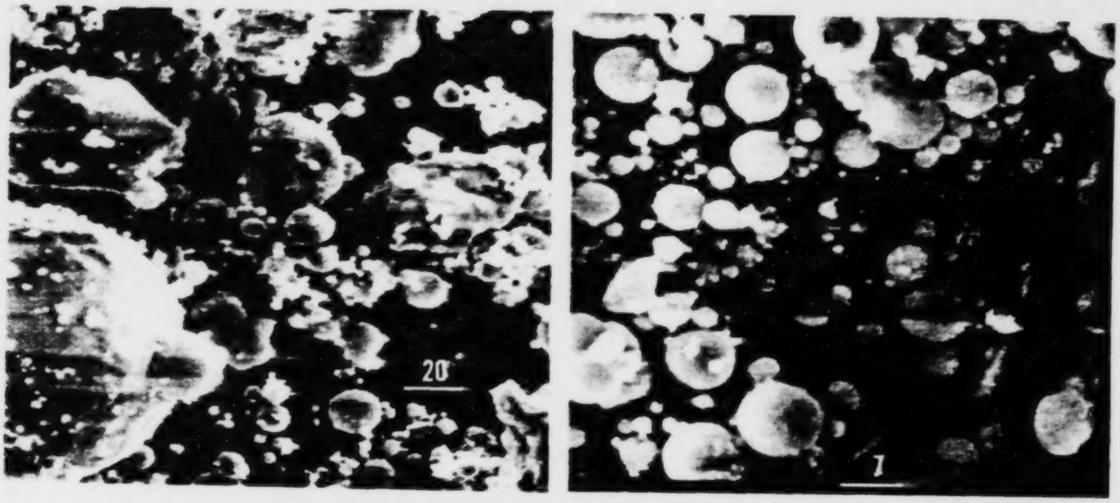
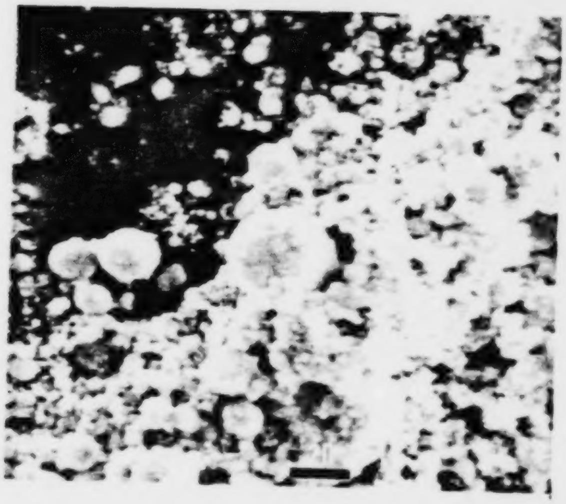
[1] Sphericity and roundness are two common features of particle morphology. Sphericity is defined as the ratio of the surface area of a sphere of the same volume as the particle under examination to the actual surface area of that particle. Roundess may be expressed as the ratio of the average radius of curvature of the several corners or edges to the radius of curvature of the maximum inscribed sphere. By definition a perfect shape will have a roundness of 1 and a sphericity of 1, the maximum values for each parameters (Pettijohn 1957).



a. Stage I

b. Stage II



c. Stage III

Figure 6. Electron photomicrographs of fly ash particles from precipitator stages I through III collected in September 1975. The scale is given by the bar in μm.

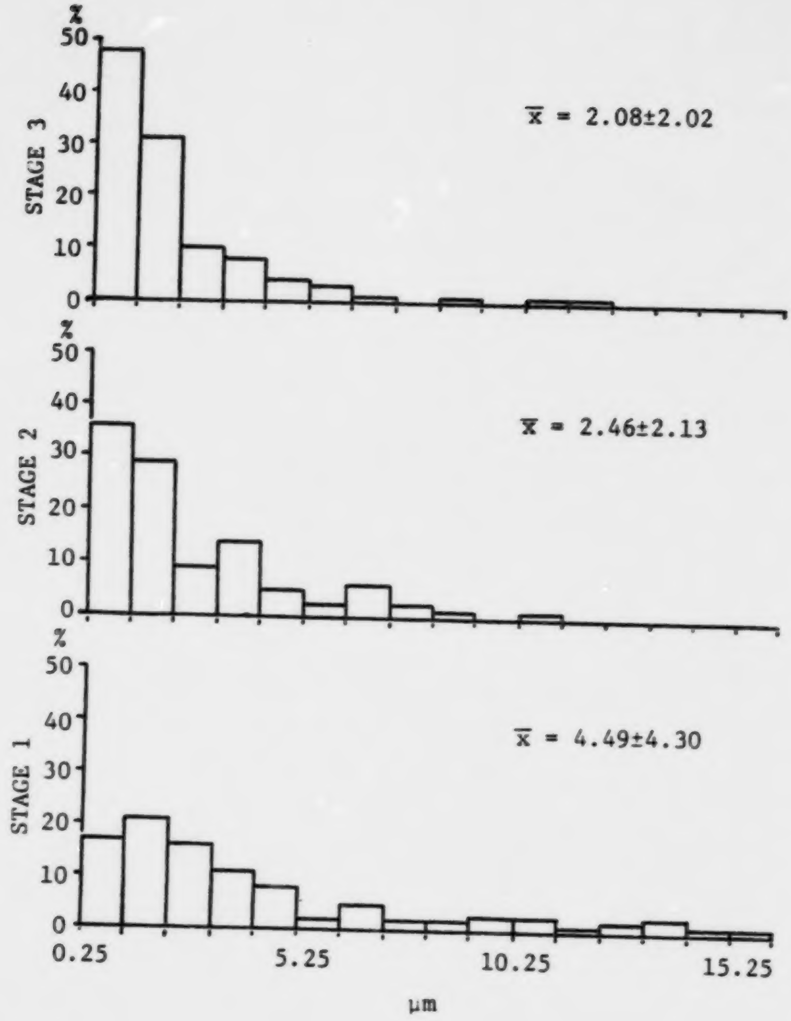


Figure 7. Histograms showing the size (in μm) distribution for fly ash from the first three stages of the precipitator from 5 September 1975.

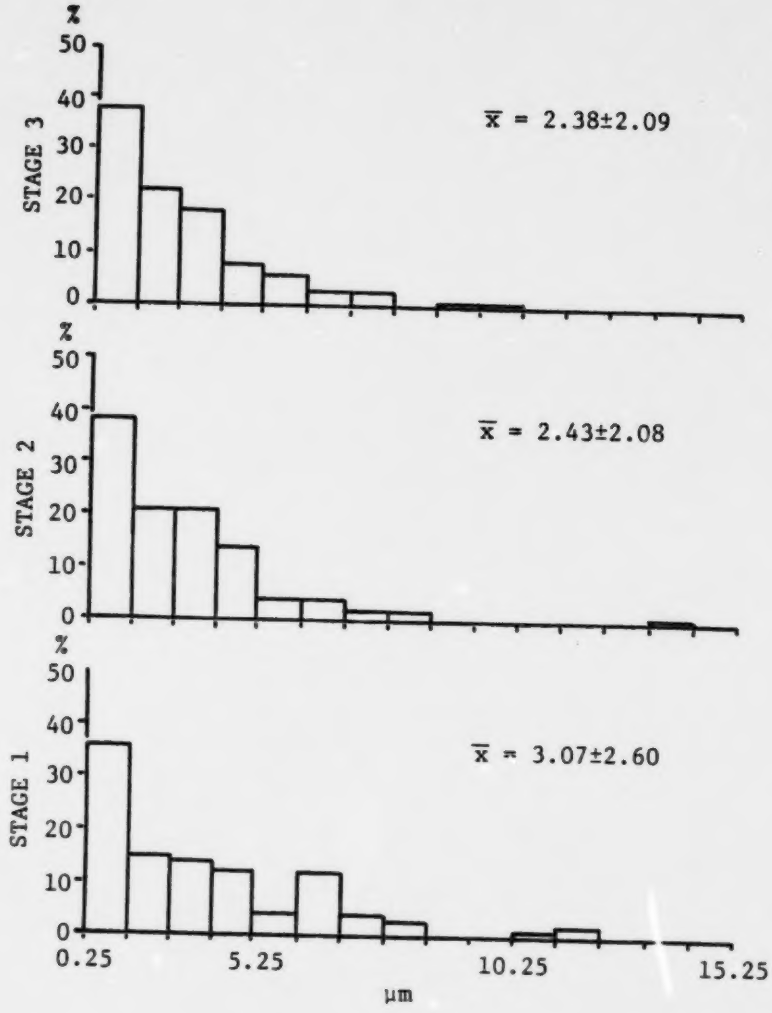


Figure 8. Histograms showing the size (in µm) distribution for fly ash from the first three stages of the precipitator from 22 April 1976.

thimbles and back-up glass filters that were used in ports within the stack testing apparatus to trap fly ash particles. A modified ASME PTC 27 test procedure was used. Thimbles 5, 6, and 9 contained some loose fly ash as well as considerably larger quantities adhering to the walls. In these samples, the loose fly ash was poured into a container and treated as a separate sample. The fly ash adhering to the walls was removed by gentle scraping with a Teflon strip.

These particles are similar in morphology and size distribution to those found in material collected in the third stage of the precipitator in April 1975. The size distribution for the stack samples collected in July 1976 is shown in Figure 9. The surface composition of the particles in these samples is given in Table 12.

TABLE 12. SURFACE COMPOSITION OF FLY ASH SAMPLES COLLECTED FROM THE PRECIPITATORS IN SEPTEMBER 1975 AND APRIL 1976 AND FROM THE THIMBLES USED DURING THE JULY 1976 STACK TESTING

	Fly ash for stages, %						
	September 1975			April 1976			
Element	I	II	III	I	II	III	Thimble fly ash, %[a] July 1976
Na	b	b	b	1	2	2	3
Mg	2	1	3	4	4	4	5
Al	31	35	30	17	14	16	12
Si	39	36	37	23	19	20	16
S	1	1	2	5	6	6	8
K	4	4	3	1	2	1	1
Ca	18	19	21	45	49	48	52
Ti, Ba	1	1	1	1	1	1	1
Fe	4	3	3	3	3	2	2

[a] Average of four samples.
[b] Not detected.

The precipitator was operating near its theoretical efficiency of 99.5% when the September 1975 samples were collected. The efficiency was considerably less, however, but at an unmeasured value when the April 1976 samples were collected. The efficiency was calculated at 98 and 88% for the stack samples collected on 9 and 14 July 1976, respectively. This calculation was based on data contained in the test report (Ziesmer 1976). During these tests the rate of particulate emissions was 475 and 2,565 kg/h with an average coal consumption of 255,000 and 266,000 kg/h containing about 8.0 and 8.4% ash, respectively.

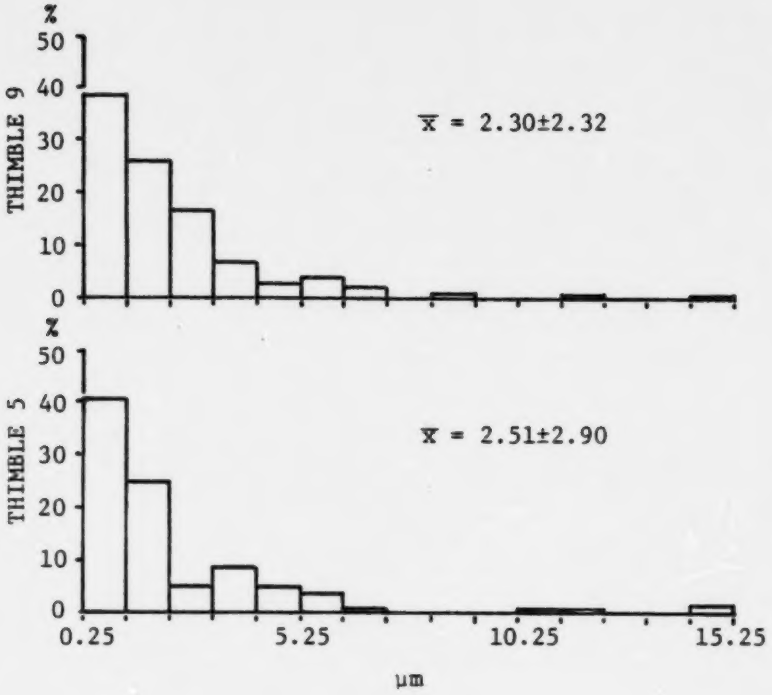


Figure 9. Histograms showing the size (in μm) distribution for fly ash from stack samples 8 and 9 collected after the precipitator.

The 1975 and 1976 samples show considerable difference in the distribution of particle sizes in the three precipitator stages. In particular, the samples collected during September 1975 show an increasing degree of separation, with respect to size, as the particle-bearing gas flows through the three stages: The first stage contains the greatest portion of large particles and the third stage contains the smallest portion. In the April 1976 samples, only small differences in particle size were observed at the three successive stages. The mean particle diameters for these two sets of samples (Figure 10) show these differences clearly. Not included in the statistical survey which determined the mean particle size were a few very large particles contained in the September 1975 samples. Even when these large particles were discounted, the September series still exhibited a wide variety of particle sizes at each stage, with a strongly decreasing mean diameter from stages I to III. The April 1976 series, on the other hand, contained material of much more uniform size with little gradation between stages.

The surface composition of the ash in the two sets of samples varied considerably. The September 1975 material was dominated by Si, Al and Ca, with trace amounts of Mg, K, Fe, S, Ti, and Ba. The April 1976 ash, however, was dominated by Ca, which accounted for nearly 50% of the surface elemental composition. Silica, Al, and S were present in the April samples, with S having surface concentrations about three times as great as those in September 1975 samples. Sodium was detected easily in the April samples, but not in September. Little difference occurred in bulk composition between the two sets of samples. The different concentrations of Ca, K, and Fe indicate that the coal burned in April 1976 had a slightly different composition from that of September 1975. Apparently, slight differences in bulk composition can lead to marked differences in surface composition. It is interesting to note that the September material was collected during the only period in which the precipitators operated at design capacity without addition of a conditioner while the generating station was operating at maximum power.

The average resistivity of the Columbia fly ash is 10^{10} ohms/cm and the normal temperature of the flue gases in the precipitators is 132°C (Ziesmer, Wisconsin Power and Light Co., personal communication). Comparing these values with information presented in Figure 3 might lead to the conclusion that the Columbia fly ash is high in Na. This is not the case, however, since the Portage ash is extremely high in Ca, at least on the surface of the particles, which leads to speculation that the high Ca is acting as a charged conductor, reducing the resistivity of the ash and making it difficult to collect in the electrostatic precipitators.

The material collected in the stack is similar to the stage III sample collected in April 1976 in terms of particle surface composition although the stack samples have slightly higher Ca and S concentrations. The bulk composition of the stack fly ash is similar to that from the third stage samples from April 1976, with one important exception: The material from the stack contained 4.0% Fe and 0.32% Na, whereas that from the precipitator contained 3.4% Fe and 0.20% Na. This accounts for the stack ash escaping

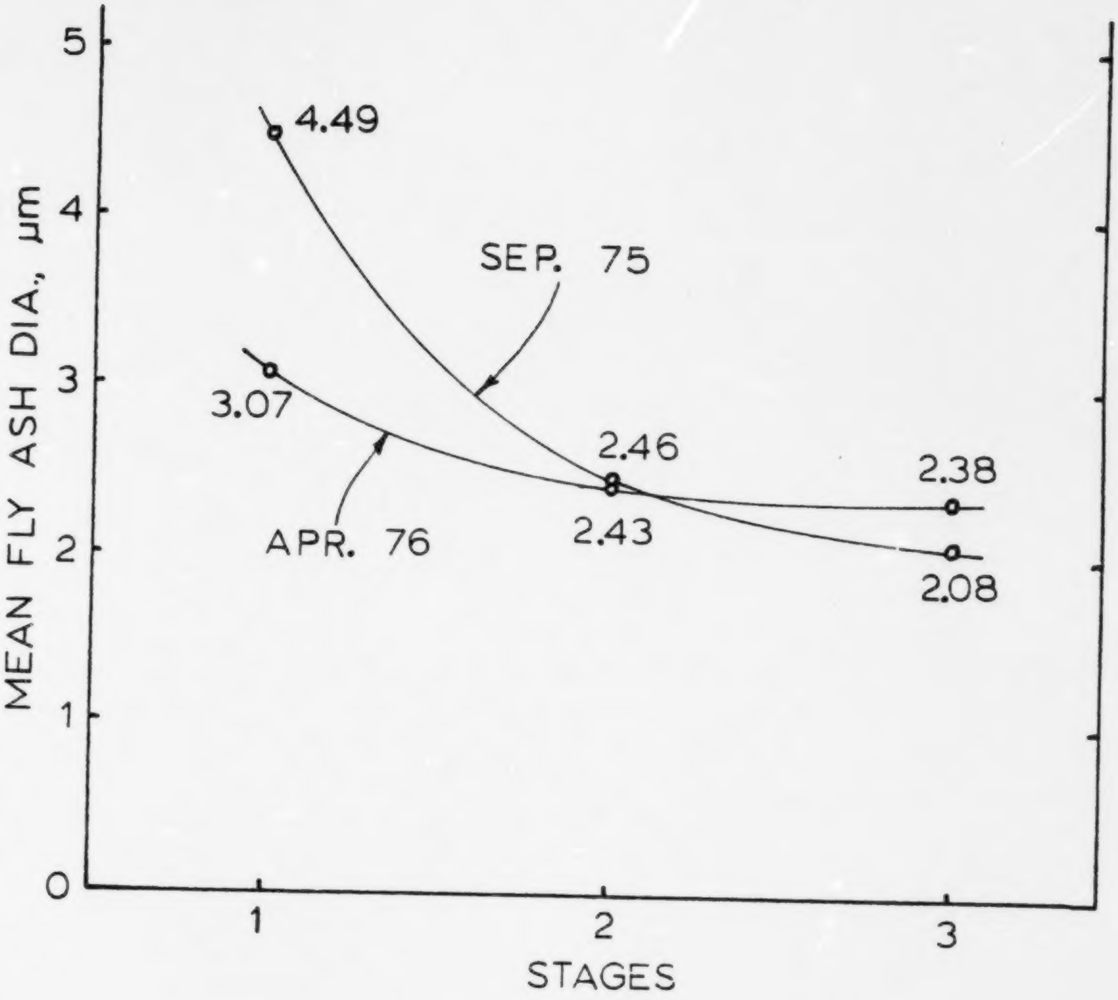


Figure 10. Comparison of mean grain sizes (in µm) of fly ash collected from precipitator stages I through III at Columbia I during September 1975 and April 1976.

the electrostatic precipitators since high concentrations of Na and Fe lead to lower values of particle resistivity.

Distribution of particle sizes and concentrations of elements for the stack samples are similar to those of stage III of the precipitator. An important exception is the concentration of Se which is much higher in the stack samples, implying that this volatile element does not condense on fly ash at temperatures characteristic of the flue gas.

Fly Ash from the Ash Pond

Fresh fly ash consists mostly of glassy, amorphous material. Small amounts of quartz, anhydrite, magnetite, hematite, periclase and CaO were identified in the fresh fly ash by x-ray diffraction. Many new minerals appear after the fly ash is mixed with water and slurried to the ash pond. A complete list of the minerals identified by x-ray diffraction in the samples collected from the ash pond is given in Table 13. Some of these minerals, especially the calcium aluminate sulfates and calcium aluminate silicates contribute significantly to the strength and properties of Portland cement. The hardness of the fly ash in the ash pond must result from the formation of these minerals. Future research should explore the reactions of fly ash with water to form a cement-like material, especially for ashes containing a high content of lime, so that new and potentially valuable uses for fly ash can be developed. Also, these reactions may result in reducing pollution by SO_4 contained in the ash effluent discharged from ash ponds since the calcium aluminate sulfates are much less soluble than gypsum.

TABLE 13. MINERALS IDENTIFIED BY X-RAY DIFFRACTION IN SAMPLES OF FLY ASH FROM THE ASH POND

Name	Density (g/cm^3)	Composition
Calcite	2.71	$CaCO_3$
Ettringite	1.73	$Ca_6Al_2(OH)_{12}(SO_4,SiO_4,CO_3)_3 \cdot 26H_2O$
Faujasite	1.92	$Na_2O \cdot Al_2O_3$
Gaylussite	–	$Na_2Ca(CO_3)_2 \cdot 5H_2O$
Gypsum	2.32	$CaSO_4 \cdot 2H_2O$
Hematite	5.26	Fe_2O_3
Magnetite	5.20	Fe_3O_4
Mirabilite	1.46	$Na_2SO_4 \cdot 10H_2O$
Mullite	3.15	$3Al_2O_3 \cdot 2SiO_2$
Quartz	2.65	SiO_2
Thenardite	2.68	Na_2SO_4

The morphology of the grains of fly ash from the ash pond is similar to that of fresh fly ash. The major difference is the proportion of broken, hollow spheres. This type of grain is more abundant in fly ash from the ash pond than the fresh fly ash. The water in the ash pond apparently causes many of the hollow fly ash grains to break, making them easier to recognize. After long periods of time, the fly ash grains tend to weather concentrically. This is especially noticeable for the grains of fly ash found in the suspended particulate matter from the drainage system of the ash pond.

Suspended Particulates and Water from the Ash Pond and its Drainage System

Concentrations of elements measured in samples of suspended particulate matter from the ash pond and its drainge system are given in Table 14. The composition of the flyash discharged to the ashpond (Sample 1 in Table 14 is almost the same as that of the fly ash in the last two stages of the precipitator (Tables 6 through 9). However, the concentrations of most trace elements in the suspended material are less (Sample 2 in Table 14) than in the total fly ash. An exception is Ca which has almost doubled in concentration found for the total fly ash. The fraction that is < 1 mμ has even lower concentrations of all elements except As. Sample 4 was collected from the outfall of the ash pond. The concentrations of most elements are even lower in this sample. Important exceptions are Ba and Cr. Barium is present at a concentration three times that measured for the total fly ash and Cr is present at a concentration of 2.5 times that found in total fly ash. It may be that the high pH of the ash pond water--9.5 to 10.1--encourages dissolution of Ca, Ba and Cr from the fly ash and the formation of finely divided material that remains in suspension. The pH of the system is high enough that Cr may be in the form of the CrO_4 ion, the most toxic form of Cr.

The concentrations of As and Fe are high in the sample from the mint drain (Sample 5). This may result from the suspected low redox potential of this water which is situated in an area of peaty soils and originates in marshland. The concentration of Ca is below detection limits for this sample. Samples 6, 7, and 8 were collected in the ashpit drain below the point where the mint farm drain joins it. These samples have characteristically high Fe concentrations which probably reflect the influence of the mint drain. The high concentration of Cr in the ashpit drain supports the hypothesis that it is being selectively dissolved from the fly ash and oxidized to CrO_4, which is soluble. It is then reduced to Cr^{3+} and precipitated as $Cr(OH)_3$ after the water from the ash pond mixes with water from the mint drain which has a lower pH.

Concentrated H_2SO_4 is added to the water discharged from the ash pond until its pH is lowered to approximately 7. This assures compliance with the conditions of the discharge permit for the station. The addition of the SO_4^{2-} causes $BaSO_4$ to precipitate. This effect is evidenced by the large increase in Ba concentration in sample 4 (Table 14).

TABLE 14. CONCENTRATIONS (μg/g) OF TRACE ELEMENTS IN SAMPLES OF SUSPENDED PARTICULATE MATTER COLLECTED FROM THE ASH POND AND ITS DRAINAGE SYSTEM[a]

	Site[b]							
	1 and S.D.[a]	2	3	4	5	6	7	8
As	29 ± 3	29	41	13	48	18	19	18
Ba	6,600 ± 200	4,700	2,700	17,000		1,300	1,000	1,200
Br								
Ca	120,000 ± 11,000	240,000	44,000	11,000		36,000	32,000	
Cd								
Ce	90 ± 0.6	46	19	14	9.0	11	15	18
Cr	53 ± 1	30	36	130	110	740	1,200	1,300
Cs	5.4 ± 0.1	2.2	1.6	1.4		1.6	1.3	
Co	11 ± 0.1	5.6	2.8	2.5	4.8	2.4	3.3	2.3
Eu	1.4 ± 0.03	0.60	0.27	0.20		0.19	0.25	0.48
Hf	8.5 ± 0.2	3.2	1.1	0.77		1.1	1.2	
Fe	44,000 ± 200	18,000	13,000	7,900	46,000	34,000	43,000	45,000
K	2,900 ± 300	1,300	1,100	1,700		3,300	4,900	6,100
La	57 ± 1	26	12	7.7	4.3	5.1	7.0	9.6
Lu	0.66 ± 0.01	0.33	0.20	0.17		0.09	0.11	0.09
Mn								
Na	4,000 ± 50	1,600	770	820	1,900	1,100	1,600	3,100
Nd	44 ± 6	21	14	13				
Rb	13 ± 1	8		5				
Sb	20 ± 1	9.0	7.0	5.0		4.7	5.0	4.8
Sc	14 ± 0.01	6.3	2.3	1.7	1.6	1.6	2.1	2.4
Se	0.21 ± 0.04		0.21		0.33	0.18		
Sm	8.5 ± 0.1	4.0	2.2	1.4	0.82	1.0	1.2	1.5
Tb	1.6 ± 0.05	0.66	0.25	0.15		0.11	0.11	
Th	33 ± 0.2	14	4.8	3.1	1.5	1.8	2.3	2.3
U	10 ± 0.7	7.1	9.0	2.4		0.80	0.96	2.0
Yb	3.8 ± 0.2	1.6	0.37	0.36		0.33	0.60	0.55
Zn	80 ± 3	52	70	38	100	100	96	120
pH	10.1	9.5		9.2	7.2	7.6	8.2	8.2

[a] The analytical uncertainties associated with the values in the first column represent one standard deviation based on counting statistics.

[b] The samples were collected at the following locations: 1--fly ash suspended in water as it is pumped into the ash pond; 2--suspended material in water collected next to the delta of fly ash in the ash pond; 3--a subsample of #2; this sample contains only particles < 1 μm as determined by Stoke's law; 4--suspended material from ash pond water as it enters the ditch draining from mint farms; 5--suspended material from the water in the mint drain above the entry point of the water from the ash pond; 6--suspended material in the water about 1 mile below the confluence of the mint drain and ash pond drain; 7--same as #6 but collected about 2 miles below the confluence; 8--same as #6 but collected about 3 miles below the confluence. The drainage ditch enters the backwater of the Wisconsin River at this point.

The concentrations of selected elements in the water samples are given in Table 15. The concentrations of soluble Al, Ba, Ca, Cr, Sr, and SO_4^{2-} are much higher in water from the ash pond and its drainage system than they are in the mint drain or in the Wisconsin River. Also, most or all of the Cr is present as chromate (CrO_4). The concentrations of Na, K, Cl, and Br are about the same at all of sample locations. Concentrated H_2SO_4 is added to the ash effluent; this is reflected in an increase in SO_4 concentration and decrease in pH in sample 2 compared to sample 1. The increase in elemental concentrations is of concern because excessive concentrations of many elements can be toxic to organisms. Chromium generally is considered to be moderately toxic when present as Cr^{3+}, but the toxicity of CrO_4--the form of Cr present in the ash pond--is considerably greater. Barium is only slightly toxic, especially when it is present as $BaSO_4$. High concentrations of soluble Al are toxic to fish because Al precipitates and interferes with the function of their gills.

TABLE 15. REPRESENTATIVE ANALYSES OF WATER SAMPLES COLLECTED FROM THE FLY ASH POND AND ITS DRAINAGE SYSTEM ON 1 APRIL 1976[a]

	Sample no.				
	1	2	3	4	5
pH	11.2	8.8	7.2	7.6	7.8
Cl, mg/liter	12±0.6	12±0.5	6.5±0.1	14±0.6	11±0.6
Br, μg/liter	19±6	---	19±1	23±5	22±4
Na, mg/liter	17±0.1	17±0.1	3.5±0.2	12±0.1	7.4±0.03
K, mg/liter	2.5±0.3	1.9±0.3	1.1±0.1	4.7±0.4	2.0±0.2
Ca, mg/liter	90±10	90±20	40±10	70±10	<20
Sr, mg/liter	4.5±0.1	3.6±0.2	<0.1	2.5±0.1	<0.2
Ba, μg/liter	730±60	450±70	<75	380±50	<50
Cr (total), μg/liter	20±2	15±4	<1	16±2	<1
CrO_4, μg/liter	21	22	<1	11	<1
Al, mg/liter	3.1	0.42	<0.001	0.32	<0.001
SO_4, mg/liter	180	220	18	150	10

[a] Sample locations are: 1. Outfall of fly ash pond, 2. after addition of H_2SO_4 but before mixing with mint drain, 3. mint drain, 4. after confluence of mint and ash pond drain, 5. water from Wisconsin River. All of the samples were filtered through a 0.45-μm membrane filter before analysis. Uncertainties represent one standard deviation based on triplicate analyses.

The concentrations of several elements, especially Ca, Ba, and Cr, are higher in the water that is discharged from the ash pond than can be supported in waters from natural environments. These elements and probably others precipitate as the pH of the water reaches more neutral values. The presence of elevated concentrations of some elements in the drainage system of the ash pond suggests that organisms inhabiting this system may accumulate high concentrations of these elements.

Aerosolic Dust

The flux of fly ash in the environment, as estimated from the proportion of fly ash contained in the material collected in fallout buckets, is given in Table 16. The values for the flux of fly ash should be considered as estimates because they were calculated by multiplying the fractional abundance of fly ash in the samples by the weight of the sample. This approach assumes that all particles in the sample have the same size and density, which is not the case since fallout buckets tend to favor larger particles. Therefore the samples collected in buckets probably do not provide accurate representation of the distribution of particles in the atmosphere. Aerosols are removed from the atmosphere by wet deposition, sedimentation, impaction, and diffusion. Droplets also collect particles < 0.1 μm by means of Brownian motion and water vapor gradients. Falling raindrops also can collect particles by impaction.

Falling particles of fly ash and other dusts accelerate until terminal velocity is reached. This velocity is dependent on gravitational acceleration, the viscosity of the air, and the particle's density, size, and surface roughness. From calculations of terminal velocities, it is apparent that deposition is important only for particles > 5 μm in diameter.

Particles with a diameter of < 0.5 μm are removed by Brownian diffusion through the stagnant air layer (0.1 to 10 mm thick) at an environmental surface. Particles > 0.5 μm are removed by impaction through the stagnant layer. Aerosolic dust buckets remove particles mainly through impaction and sedimentation, with minor contributions from wet deposition and diffusion.

The calculated flux of fly ash in the aerosolic dust buckets is generally less than several tenths of a $mg/m^2/day$, except for occasional samples where flux is several $mg/m^2/day$. It appears, with occasional exceptions, that only background quantities of fly ash and other materials are deposited and collected. According to the meteorological data interpreted by Ragland (personal communication), the plume from the stack would be expected to sweep over one particular spot in the environment surrounding the power plant for about 12 h/month. Therefore, only small amounts of ash, if any, from the Columbia Generating Station could be expected in the samples collected at any site during any given series of months.

This hypothesis was tested for samples collected at site P-24 between November 1974 and January 1976. These samples span several months before and after Columbia I started operations in April 1975. At that time, Columbia I was the only major station burning a high Ca coal in Wisconsin.

TABLE 16. FLUX OF FLY ASH INTO THE ATMOSPHERE AS MEASURED BY THE CONTENT OF FLY ASH IN FALLOUT BUCKETS[a]

Collection date	Flux of fly ash ($mg/m^2/day$)	Total no. of grains counted	Fly ash (%)
	Site P-24		
11/17/74	--	1,374	18
12/14/74	0.62	2,671	18
01/13/75	--	2,955	13
02/11/75	0.47	3,617	8.2
03/13/75	0.32	2,894	12
04/14/75	0.95	1,428	14
05/12/75	0.54	7,974	4.6
07/07/75	3.2	4,815	32
08/05/75	0.78	3,110	9.4
09/05/75	0.57	3,447	5.9
10/06/75	0.54	2,652	6.9
10/24/75	0.97	2,321	9.0
11/21/75	0.63	2,291	7.2
12/19/75	--	2,651	7.1
01/23/76	0.74	3,392	16
	Site D-12		
07/27/76	1.8	1,017	9.5
09/25/76	0.37	1,092	4.1
10/25/76	0.29	1,025	2.0
12/08/76	1.1	1,206	20
02/23/77	0.07	1,059	2.8
04/22/77	--	1,014	2.4
07/11/77	0.62	1,013	2.9
08/11/77	0.54	1,243	3.9
09/12/77	0.40	1,114	6.2
10/07/77	0.13	1,062	0.7
11/11/77	0.23	1,008	6.4
12/16/77	0.22	1,035	4.2
02/24/78	0.04	1,051	2.6
05/01/78	0.05	1,036	0.8
	Site D-4		
10/24/75	--	1,103	0.6
11/21/75	--	1,062	1.1
01/23/76	0.33	1,038	7.9
03/11/76	--	1,022	30
04/22/76	1.8	1,026	12
05/25/76	--	1,014	3.4
06/29/76	0.72	1,038	3.9

(continued)

TABLE 16 (continued)

Collection date	Flux of fly ash ($mg/m^2/day$)	Total number of grains counted	Fly ash (%)
07/27/76	1.6	1,035	15
08/25/76	0.23	1,007	3.2
09/25/76	0.48	1,032	6.2
10/25/76	0.89	1,024	6.6
12/08/76	0.16	1,079	3.4
02/23/77	0.10	1,017	3.2
04/22/77	--	1,026	4.1
07/11/77	1.9	1,039	9.2
08/11/77	0.49	1,055	5.7
10/07/77	0.66	752	15
11/11/77	0.42	821	13
12/16/77	0.07	992	2.3
03/24/78	0.09	1,028	5.1
05/01/78	0.26	1,019	3.5
	Site P-13		
11/17/74	0.07	1,131	2.3
12/14/74	0.07	1,493	3.0
02/11/75	0.11	1,316	1.4
03/13/75	0.09	1,094	6.6
04/14/75	0.16	1,026	2.8
07/07/75	0.30	1,038	3.2
09/05/75	0.44	1,205	2.6
10/06/75	0.10	1,068	1.8
10/24/75	2.9	1,052	4.2
11/21/75	0.25	1,016	3.9
01/23/76	0.14	1,119	4.9
03/11/76	0.37	1,024	7.8
07/27/76	0.78	1,026	4.2
09/25/76	0.20	1,034	2.3
10/25/76	0.40	1,022	3.6
12/08/76	0.85	1,117	3.8
02/23/77	0.10	1,008	4.2
04/22/77	--	1,092	0.7
08/11/77	0.77	1,206	7.8
09/12/77	0.10	1,143	2.2
10/07/77	0.26	1,695	6.0
11/11/77	0.32	1,994	5.4
12/16/77	0.08	1,085	2.6
	Site C-26		
11/17/74	0.12	1,374	2.9
12/14/74	0.02	1,028	1.3

(continued)

TABLE 16 (continued)

Collection date	Flux of fly ash ($mg/m^2/day$)	Total number of grains counted	Fly ash (%)
02/11/75	0.14	1,223	4.6
03/13/75	0.27	1,104	21
04/14/75	0.11	1,065	2.1
05/12/75	0.74	1,032	7.4
06/10/75	0.45	1,024	4.2
07/07/75	0.89	1,129	8.1
08/05/75	0.14	1,114	1.9
10/06/75	0.22	1,055	5.3
10/24/75	0.18	1,133	2.2
11/21/75	0.40	1,094	8.1
01/23/76	0.08	1,077	5.4
03/11/76	0.77	1,049	16
07/27/76	0.45	1,004	4.8
09/25/76	0.15	1,015	1.4
10/25/76	0.32	1,008	2.4
12/08/76	0.22	1,102	7.7
02/23/77	0.05	1,023	2.6
07/11/77	1.4	1,075	12
08/11/77	0.33	1,127	3.4
09/12/77	0.05	1,038	0.8
10/07/77	0.67	878	13
11/11/77	0.56	1,111	9.6
12/16/77	0.04	1,062	1.2
03/24/78	0.03	1,227	2.9
	Site W-5		
12/14/74	0.15	1,237	6.2
02/11/75	0.11	1,224	2.9
03/13/75	0.04	1,076	2.0
04/14/75	0.29	1,329	3.6
05/12/75	0.31	1,058	4.6
07/07/75	0.75	1,033	1.9
08/05/75	0.15	1,005	1.5
09/05/75	0.23	1,022	3.0
10/06/75	0.30	1,093	7.4
10/24/75	0.15	1,062	1.8
11/21/75	0.24	1,104	3.1
01/23/76	0.75	1,417	17
03/11/76	0.19	1,253	3.2
04/22/76	0.74	1,075	4.4
05/25/76	--	1,022	2.6
07/27/76	0.54	1,008	6.5
09/25/76	--	1,026	4.4

(continued)

TABLE 16 (continued)

Collection date	Flux of fly ash ($mg/m^2/day$)	Total number of grains counted	Fly ash (%)
10/25/76	0.45	1,062	4.1
12/08/76	0.10	1,026	2.5
02/23/77	0.24	1,102	11
07/11/77	5.7	1,035	19
08/11/77	0.19	1,024	5.1
09/12/77	0.26	1,229	5.7
10/07/77	0.29	1,742	6.0
11/11/77	0.38	1,435	7.6
03/24/78	0.04	1,134	2.6
05/01/78	0.16	1,046	3.3
Site FW-34			
07/27/76	0.40	1,051	3.7
09/25/76	0.25	1,018	2.0
10/25/76	0.01	1,016	1.7
12/08/76	0.16	1,038	2.7
02/23/77	0.03	1,034	0.8
Site Larsen's			
08/25/76	1.2	1,040	13
09/25/76	0.44	1,026	5.5
10/25/76	0.10	1,034	0.7
12/08/76	0.06	1,047	1.2
02/23/77	0.13	1,064	5.3
08/11/77	1.5	1,098	16
09/12/77	0.04	1,044	0.6
12/16/77	0.12	1,137	3.7
03/24/78	0.03	1,017	1.7

[a] Each collection period was about 30 days ending on the date shown.

It should be possible to identify the Columbia I fly ash particles in these samples by their composition.

Samples of fly ash from the last stage of the precipitator were analyzed by x-ray fluorescence with the electron microprobe to determine the relative concentrations of elements on the surface of fly ash particles. The results (Table 17) reveal high concentrations of Ca on the surfaces of fly ash particles from the Columbia Generating Station. Analyses of samples collected at site P-24 prior to April 1975 show that few if any fly ash particles have surface compositions similar to those from the power plant. The results of these analyses indicate that fly ash from the Columbia Generating Station can be recognized from the compositional characteristics given in Table 18.

TABLE 17. TYPICAL SURFACE COMPOSITIONS OF FLY ASH COLLECTED IN SEPTEMBER 1975 AND APRIL 1976 FROM STAGE III OF THE PRECIPITATOR

Element	September 1975 (%)	April 1976 (%)
Na	not detected	2
Mg	3	4
Al	30	16
Si	37	20
S	2	6
K	3	1
Ca	21	48
Ti, Ba	1	1
Fe	3	2

TABLE 18. SURFACE COMPOSITIONS OF NON-COLUMBIA AND COLUMBIA FLY ASH COLLECTED IN FALLOUT BUCKETS AT SITE P-24

Non-Columbia fly ash	Columbia fly ash
Si > Al	Si > Al
K > Ca	Ca > K
S present	S not present
Cr, Mn, Co present	Cr, Mn, Co present
Na, Mg present	Na, Mg not present

The surface composition of the fly ash samples collected in the buckets varies greatly, especially when compared to the relatively small variations in composition of the material collected in the precipitators. Evidence indicates that two distinctly different sets of fly ash particles enter the environment surrounding the Columbia Generating Station. The data in Table 18 indicate that the fly ash in samples collected prior to the operation of the power plant contained higher concentrations of Si than Al, higher concentrations of K than Ca, and detectable levels of S, Cr, Mn, Co, Na, and Mg. Fly ash from Columbia I, however, has a very different overall composition. Silicon and Al are similar in concentration. Calcium is present in a greater concentration than K and most of the other common elements have relatively low concentrations or are not detected.

It is possible to group the surface composition data for fly ash from the buckets into three categories: 1) Fly ash similar to that collected prior to the operation of Columbia I; 2) fly ash similar to that collected from the precipitators of the power plant; and 3) fly ash of uncertain origin characterized by either very siliceous or ferruginous compositions, both of which are found in minor abundance in the first two categories. A comparison of the amounts of ash in each of these categories, along with the fly ash flux and date of collection for site P-24 is given in Table 19.

TABLE 19. DIFFERENTIATION OF FLY ASH COLLECTED AT SITE P-24 INTO COLUMBIA AND NON-COLUMBIA FLY ASH, AND FLY ASH OF UNCERTAIN AFFINITIES

Collection date	Flux of fly ash ($mg/m^2/day$)	Columbia fly ash (%)	Non-Columbia fly ash (%)	Fly ash of uncertain affinities (%)
11/17/74	--	0	92	7
12/14/74	0.62	0	93	6
01/13/75	--	0	90	9
02/11/75	0.47	0	95	4
03/13/75	0.32	0	87	12
04/14/75	0.95	0	84	15
05/12/75	0.54	2	90	7
07/07/75	3.2	83	11	5
08/05/75	0.78	4	87	8
09/05/75	0.57	8	85	8
10/06/75	0.54	5	84	9
10/24/75	0.97	12	80	6
11/21/75	0.63	9	80	10
12/19/75	--	11	81	7
01/23/76	0.74	8	85	6

This table reveals that a substantial quantity of Columbia-type fly ash was measured at site P-24 only during July 1975, a time which corresponds to the one period when fly ash was present in a large quantity at that site. This substantiates the interpretation that this represents an instance in which the plume from the center stack passed over this area for a long enough period of time to have a notable effect at the site.

These results show that fly ash from Columbia I is deposited in the vicinity of the Columbia Generating Station and that occasional fumigations of areas by the plume or rainfall through the plume can result in high deposition rates of Columbia ash. This approach, while apparently successful, was not applied to the samples from the other sites because it is time consuming. Several hundred analyses, each requiring several minutes, were required for each sample.

The concentration of trace elements varies from month to month in the samples collected with fallout buckets. Figure 11 is an attempt to show the possible effects that fly ash might have on the concentrations of trace elements in the material collected. This figure is a comparison diagram giving the ratio of the concentration of each element in the sample of interest to the concentration of the same element in the soil surrounding the collecting bucket. The wide bars give the ranges of such ratios for the stack samples and the narrow bars with short, horizontal bars at the ends give the range of ratios for aerosolic dust collected monthly from 12 May to 6 October 1976. A ratio of 1 signifies that the element is present in the same concentration in the sample and the local soil.

The results in Figure 11 indicate that the samples collected in buckets have concentrations of most trace elements similar to those of the local soil. Elements which show significantly higher concentrations in the aerosolic dust are Br, Hg, Sb, and Se, and to a lesser extent Th, U, and Zn. Some of this enrichment may be the result of fly ash. For example, the concentrations of Sb, Se, Th, and U are significantly higher in fly ash than in soil or aerosolic dust. The source of Hg is not known but it is definitely not from the fly ash (Tables 6 through 11). From these data, it can be concluded that the concentrations of most elements in the fly ash and aerosolic dust are similar to those in soils. It is not known if the concentrations of those elements that are high in the aerosolic dust result from the effects of fly ash or if the processes that produce high concentrations of these elements in fly ash also are responsible for the high concentrations of these elements in other aerosolic dusts.

AQUATIC INVERTEBRATES

The collection sites for the tabulated results are coded by numbers according to the following scheme in this report: 1-A; 2-B; 3-BC; 4-C, 5-D; 6-E; 7-MD; 8-RRS; 9-RRL; 10-RRU (See Figure 3).

Concentrations of elements are reported in μg/g. The uncertainty associated with each value is one standard deviation--based on counting statistics. When no γ-ray peak was distinguishable above the background, the maximum element concentration was calculated by determining the minimum number of counts necessary to give a peak. The result was reported as a "less than" value.

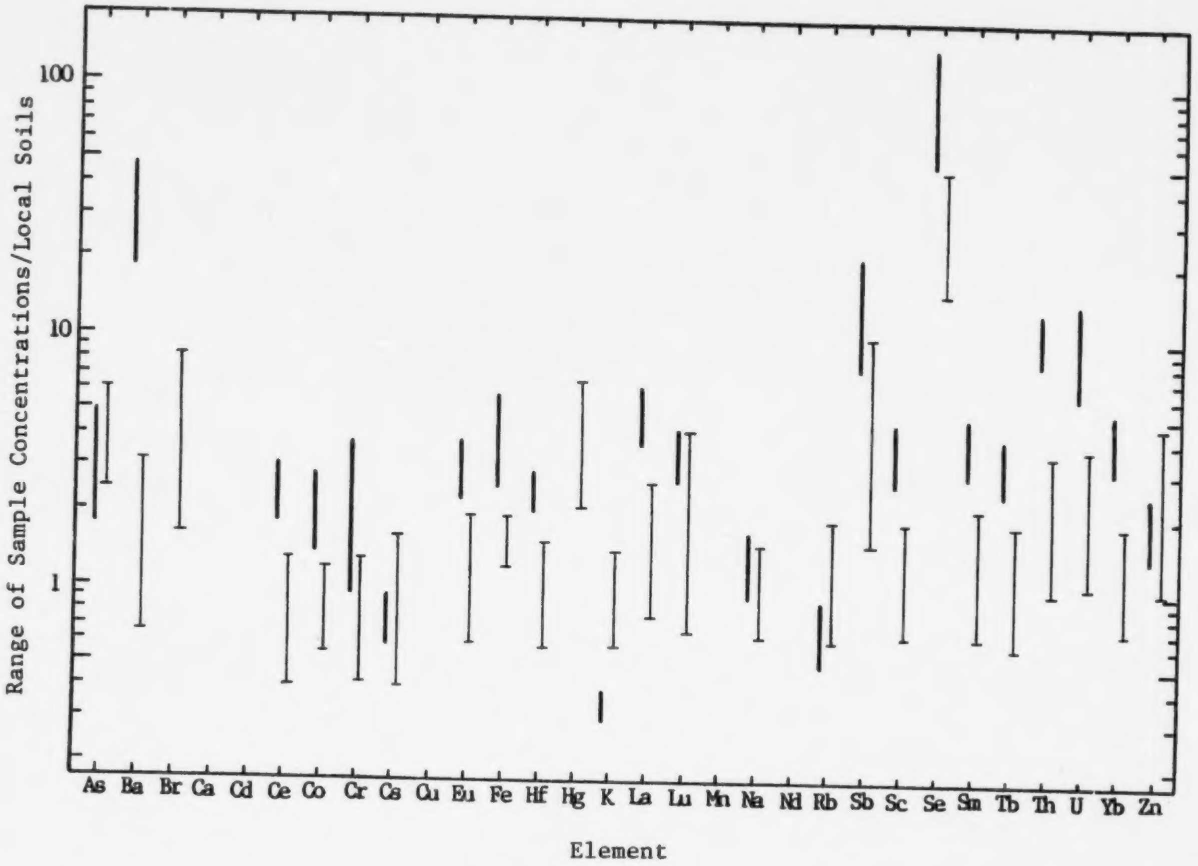


Figure 11. Elemental composition of fly ash and material collected by the fallout buckets are compared to the corresponding concentrations of elements in the local soil. The wide bars give the ranges of the ratios of concentrations for the stack samples and the narrow bars give the ranges of ratios for all sites for the five monthly samples collected in the buckets from 12 May to 6 October 1976.

Asellus racovitzai

The sampling scheme for *Asellus racovitzai* is given in Table 20. The number of organisms comprising some of the composite samples collected in 1974 and 1975 is not known. The ratio of wet:dry weight varies with organism size. For organisms with dry body weights around 0.7 mg, the ratio is 6.3; for organisms of body weight around 0.3 mg, the ratio is 4.9.

Corixidae

Two genera from the family Corixidae were analyzed. Thirteen of the 20 composite samples are composed of mixed species collections of the genus *Hesperocorixa*. Four of the composite samples are composed of single species collections of *Sigara*. The three composite samples collected on 1 July 1974 were not identified beyond the family level. Table 21 shows the sampling scheme for this family. The numbers indicate the number of composite samples analyzed for a given site and date. The average wet and dry weight ratio is 3.7 for *Hesperocorixa* and *Sigara*. When the family is taken as a single population, the standard deviation for the ratio is 0.3.

Dineutus spp.

Eight composite samples of *Dineutus* spp. were collected in 1976 and one in 1975. The 1976 samples were collected from sites RRL, BC, and D consecutively, 15 days apart beginning on 3 August 1976. The single 1975 composite sample was taken from site BC on 17 October 1975. Composite samples consisted of 4 to 8 adult specimens. The ratio of wet:dry weight for the 1976 samples is 2.9. The ratio was not determined for specimens collected in 1975.

Gammarus sp.

Three composite samples of 15 to 20 specimens each of *Gammarus* sp. were analyzed. All of the specimens were collected at site RRU on 7 October 1976, in the same location that the *Libellula* sp. were collected. The ratio of wet:dry weight is 5.0.

Hyallela azteca

Nine composite samples of *Hyallela azteca* each containing 22 to 190 organisms were analyzed. Table 22 shows the sampling scheme for this species.

Odonata

Nine samples from the family Corduliidae (*Tetragoneuria* sp.), 17 samples from the family Libellulidae (*Sympetrum* sp. and *Libellula* sp.), and one sample from the family Aeshnidae (*Anax* sp.) were analyzed. The sampling

TABLE 20. SAMPLING SCHEME FOR *ASELLUS RACOVITZAI*

Sampling site	No. of composite samples analyzed										
	1974		1975			1976		1977	1978		
	July	Oct.	Sept.	Oct.	Dec.	Jan.	Feb.	Dec.	Jan.	Feb.	March
RRS	1								1		
A		1	1	1	1						
B		1	1	2							
BC					1			4		6	3
C		1		1							
D		1				2	1				
MD				1		1	2	14	7	18	

TABLE 21. SAMPLING SCHEME FOR THE FAMILY CORIXIDAE

Sampling site	7/18/74	10/22/74	10/17/75	9/2/76	10/7/76
RRL					1
RRS	1				
A		1			
BC			1	3	
C	1	2			
D		2		4	2
RRU	1				1

TABLE 22. SAMPLING SCHEME FOR *HYALLELA AZTECA*

Sampling site	No. of composite samples analyzed			
	7/18/74	10/22/74	9/26/75	10/16/75
RRS	2			
A		1	1	1
B		1		1
C		1		
D		1		

scheme for these organisms is given in Table 23. No samples were collected before the generating station started operations. Samples collected from two sites in Rocky Run Creek and the mint drain are used as controls for the purpose of evaluating the effects of the ash effluent. Twenty of the 27 samples consist of single, whole organisms. The remaining seven samples contained two whole organisms. Ratios of wet:dry weights are not available for all of the Odonata. The ratio of 7.4 for the specimen of *Anax* sp. is somewhat higher than the 5.8 found for the specimen of *Libellula* sp. collected at site D on 2 September 1976. The determination of wet weights in Odonata larvae is complicated by the presence of anal respiratory chambers, which cause the densities of the organisms to vary (Stanford 1973).

Rana pipiens

Sixteen specimens of *Rana pipiens* (family Ranidae) were dissected and analyzed. All of the samples were collected adjacent to or in the ashpit drain on either 8 November 1974 or 13 August 1975. The frogs dried to varying extents during storage in the freezer before the dissections and hence fresh (wet) weights for whole frogs and dissected organs are not available. The length of each frog was measured before dissection as the distance from the tip of the mouth to the anus.

Sample descriptions of the frogs analyzed are presented in Table 24. Analytical samples are composed of tissue from 1, 2, or 3 frogs.

DISCUSSION

Inorganic Contamination of Samples

Samples of biological material frequently are contaminated with inorganic material (soils and sediments). This results because organisms ingest sediment while feeding and small particles of sediment can adhere to their outer layers. The effects of this contamination on values of trace elements in the organisms must be recognized before the effects of the ash effluent and other factors on the concentrations of trace elements can be determined.

Clear evidence exists that inorganic contamination of organisms occurs. Most organisms analyzed were small enough that their alimentary canal is clearly visible when they are held in front of a bright light. It is usually either partially or completely filled with opaque material. Examination of the material by scanning electron microscopy with x-ray fluorescence shows it to have high concentrations of Ca, Al, and Fe. These elements also are found in high concentrations in soils and sediments. Also, examination of the casts of the organisms shows grains of fine sand. The effects of inorganic material on the measured concentrations of trace elements in biological samples have been often ignored in studies similar to this, but the potential effects can be significant because many elements occur at much higher concentrations in soils and sediments than in biological tissue.

TABLE 23. SAMPLING SCHEME FOR ODONATA

Sampling site	Collection date				
	9/26/75	1/23/76	8/18/76	9/2/76	10/7/76
RRL					3
B	4				
BC					3
C		3			3
D				1	
RRU					3
MD		2	5		

TABLE 24. SAMPLE DESCRIPTIONS FOR *RANA PIPIENS*

Frog	Date	Site	Whole frog length (cm)	Sex	Sample analyzed[a]		
					Liver	Muscle	Skin
a	8/75	D	4.7	F	--	F20	--
b	8/75	D	4.8	F	--	F20	--
c	8/75	D	5.0	M	F6	F16,f17	f24
d	8/75	D	5.3	M	F5	F15,f18	f23
e	11/74	C	4.7	F	F2	F8	--
f	11/74	C	5.0	F	F2	F8	--
i	11/74	D	4.7	M	--	f12	--
k	8/75	A	6.6	F	F5	F15	--
m	8/75	A	7.5	F	F5	F15	--
o	11/74	A	4.9	M	F1	F7	--
q	11/74	A	4.5	M	F1	F7	--
r	11/74	A	4.7	M	F1	F7	--
s	11/74	D	6.2	F	F3	f13	--
t	11/74	D	4.5	M	F4	F9,f11	f21
u	11/74	D	5.5	M	F4	F9,f10	f22
v	11/74	D	4.5	F	F3	f14	--

[a] "F" indicates that some of the specimen's tissue was used to make a composite sample composed of tissue from more than one specimen.
"f" indicates that a sample was analyzed that was composed entirely of tissue from one specimen.

Possible procedures to remove inorganic contamination include dissection of the organisms or purging their alimentary canal with a material having a lower potential for trace element contamination. Careful dissection and removal of the alimentary canal from organisms as small as those studied here (often shorter than 5 mm) is difficult or impossible and this was not attempted. Dissection has the hazards of additional contamination from the dissecting tools and loss of body fluids or parts. Purging the alimentary canal with a non-contaminating material was not attempted because of the difficulty of finding a material that low in trace elements but ingested by the organisms. The obvious solution is to hold the organisms in clean water until they empty their guts. This was not completely successful for the organisms studied because some material remained in the gut until the organism died.

The trace element data can be used to estimate the proportion of each element in the analytical sample contributed by contamination. Several elements measured are not normally active in biochemical systems, including the rare earth elements (REE) and Sc, Th, and Hf, which occur as large ions with charges of +3 or +4. Concentrations of these elements are greater in soils and sediments than in biological samples. If their presence in biological samples results from contamination by soils and sediments, the concentrations of each should correlate significantly with the concentrations of other elements resulting from contamination (Table 25 and Figures 12 to 14). The number of samples used for each correlation analysis varies with element because the concentrations of some of the elements are below detection limits. Concentrations of the elements mentioned previously together with Co and Fe show highly significant correlations (Table 25). Although Co and Fe are biochemically active, they occur with the above group of elements because their concentrations in biological tissues are so low that small amounts of inorganic contamination can greatly affect their measured concentrations.

The element which best represents the extent of inorganic contamination is Sc for several reasons. From Table 25 and Figures 12 to 14 it can be seen that the Y-intercept is either 0 or a small positive value, suggesting that some elements can be taken up by organisms in small amounts without contamination. If Sc and the element correlated with Sc were present solely as the result of contamination, all intercepts would be 0. The small positive values for the Y-intercept are best illustrated by Co in Figure 14, since Co is an essential element. The values of the intercept of La and Sm are essentially 0, which would be expected if La, Sm, and Sc occur solely from contamination. Of the three elements, Sc was selected for comparison because the analytical procedures are especially accurate and sensitive.

Concentrations of Sc in organisms can be used to estimate relative amounts of inorganic materials contained in the sample. The mean concentrations of Sc in the invertebrate samples are given in Table 26 together with the number of samples with mean Sc concentrations > 0.01 and < 0.1 μg/g. Concentrations of Sc in *Dineutus* spp. are one or two orders of magnitude lower than those in the other invertebrate samples. Four of the 9 composite samples of *Dineutus* spp. have Sc concentrations below detection limits (< 0.002 μg/g, 95% confidence limits), the five composite samples

TABLE 25. CORRELATION ANALYSES OF Sc WITH SEVERAL ELEMENTS FOR ALL ORGANISMS ANALYZED[a]

Element	N[b]	R	Level of significance	Equation: $y = bx + a$	95% confidence interval of Y-intercept
Ce	31	0.83	0.001	$y = 6.40x - 0.0083$	$-0.800 \leq y \leq 0.784$
Co	75	0.81	0.001	$y = 1.56x + 0.129$	$-0.085 \leq y \leq 0.343$
Eu	59	0.84	0.001	$y = 0.114x + 0.008$	$-0.005 \leq y \leq 0.022$
Fe	71	0.83	0.001	$y = 340x + 201$	$-765 \leq y \leq 1167$
Hf	32	0.32	0.10	$y = 0.340x + 0.112$	$-0.079 \leq y \leq 0.303$
La	49	0.79	0.001	$y = 3.08x + 0.01$	$-0.402 \leq y \leq 0.422$
Sm	38	0.80	0.001	$y = 0.491x + 0.002$	$-0.063 \leq y \leq 0.068$
Tb	10	0.58	0.10	$y = 0.044x + 0.008$	$-0.010 \leq y \leq 0.026$
Th	40	0.85	0.001	$y = 0.831x + 0.021$	$-0.069 \leq y \leq 0.115$

[a] The correlations are based on the data from all taxons and samples irrespective of sampling site and date.

[b] N is number of samples used in calculating the regression.

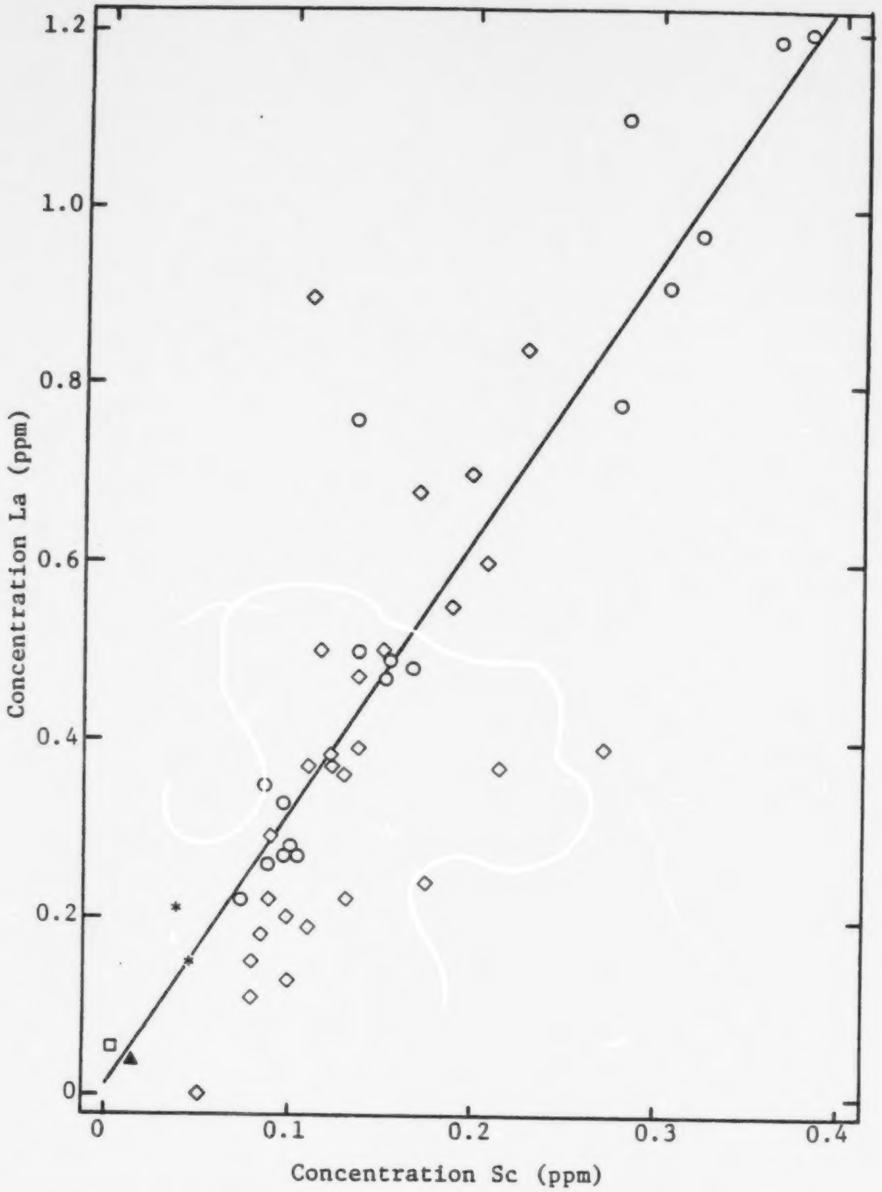


Figure 12. Relationship between concentrations of La and Sc for several organisms. The line corresponds to the least squares regression fit.

◇ Odonata

○ *Asellus racovitzai*

▲ Corixidae

∗ *Gammarus sp.*

□ *Dineutus spp.*

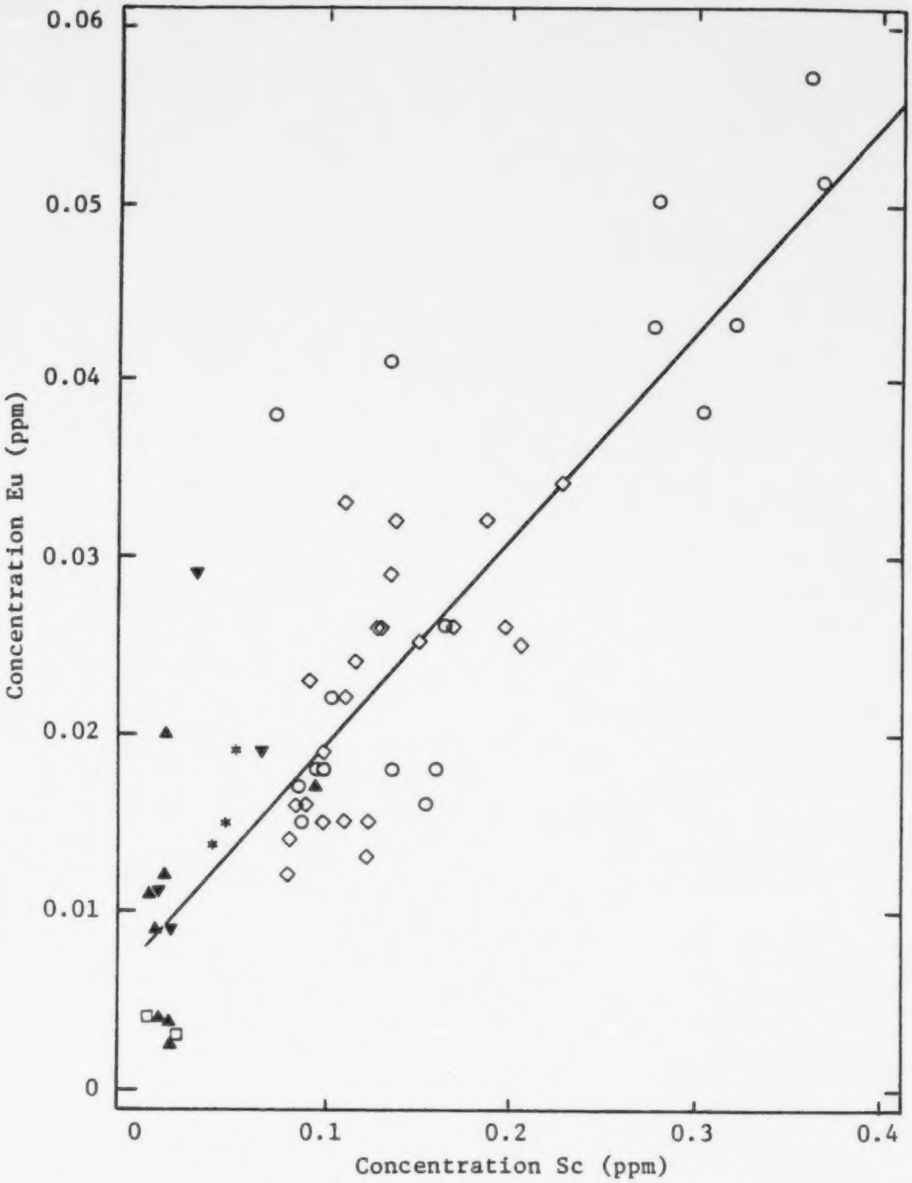


Figure 13. Relationship between concentrations of Eu and Sc for several organisms. The line corresponds to the least squares regression fit.

◇ Odonata	○ *Asellus racovitzai*
▲ Corixidae	▼ *Hyallela azteca*
□ *Dineutus spp.*	* *Gammarus sp.*

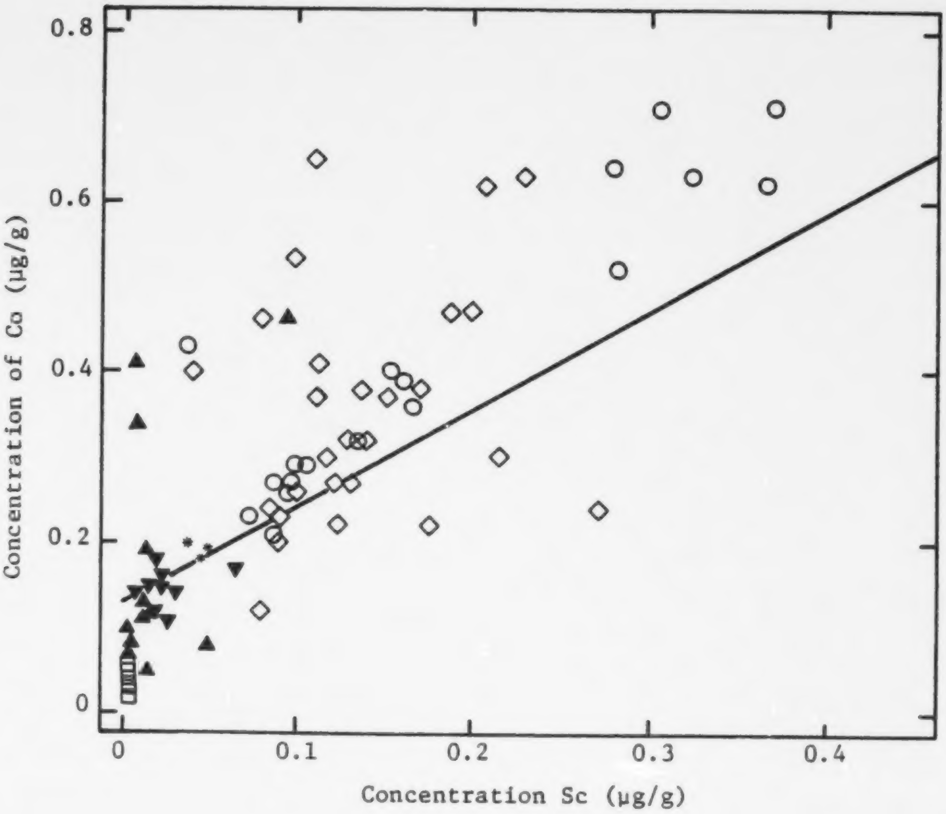


Figure 14. Relationship between concentrations of Co and Sc for several organisms. The line corresponds to the least squares fit.

◇ Odonata
▲ Corixidae
□ *Dineutus spp.*
○ *Asellus racovitzai*
▼ *Hyallola azteca*
* *Gammarus sp.*

with detectable Sc have concentrations < 0.01 μg/g. The samples of Corixidae, *Gammarus* sp., and *H. azteca* have Sc concentrations (0.1 to 0.01 μg/g) between those of *Dineutus* spp. and those of Odonata and *A. racovitzai* (≥ 0.1 μg/g). Differences in Sc concentrations are not correlated with site and date of collection.

TABLE 26. SUMMARY OF Sc CONCENTRATIONS FOR INVERTEBRATE SAMPLES

Organism	Mean ± S.D.	N	≤ 0.1 μg/g	≥ 0.01 μg/g
Asellus racovitzai	0.2 ± 0.1 (n=19)	19	16	19
Corixidae	0.02 ± 0.03 (n=12)[a]	19	1	8
Dineutus sp.	0.0021 ± 0.0007 (n=5)	19	0	0
Gammarus sp.	0.045 ± 0.006 (n=3)	3	0	3
Hyallela sp.	0.03 ± 0.02 (n=9)	9	0	8
Odonata	0.14 ± 0.05 (n=27)	27	21	27

N is number of samples analyzed.
n is number of samples with detectable Sc.
[a] One Corixidae sample (Sample C3) has a Sc concentration two orders of magnitude greater than the other Corixidae samples and is not used in calculating the mean value.

Accepting the assumption that high Sc concentrations in biological tissue reflect inorganic contamination, samples of *Dineutus* spp. are relatively uncontaminated with inorganic material while samples of Odonata and *A. racovitzai* are the most contaminated. Corixidae, *Gammarus* sp. and *H. azteca* are contaminated to an intermediate degree. It is hypothesized that the samples of *Dineutus* spp. show the least contamination because it is the only group that is not benthic. Adult *Dineutus* spp. are scavengers that swim on the water surface in large schools of mixed species (Hilsenhoff 1975). *A. racovitzai* are benthic detritivores (Chambers 1977) which ingest varying quantities of inorganic sediment along with detritus. The relatively high Sc concentrations in *A. racovitzai* are thus, in part, due to chronic ingestion of inorganic sediments. The herbivorous Corixidae and *Gammarus* sp. (Hilsenhoff 1975, Hynes 1955) probably ingest less sediment and exhibit Sc concentrations below *A. racovitzai*. *H. azteca* is described as omnivorous by Pennak (1953); algae and macrophytes are utilized to a great extent (Jackson 1912), and sediments laden with microflora (diatoms and bacteria) are ingested commonly (Hargrave 1970). Organisms utilizing the microflora laden sediment are expected to have higher Sc levels than organisms which graze on macrophytes or algae. Odonata are all carnivorous and are not expected to ingest appreciable quantities of sediment. The relatively high concentrations of Sc consistently observed with this group may result from gut contamination due to ingestion of prey species which have large amounts of sediment in their guts.

The Use of Sc Concentrations to Correct for Inorganic Contamination

The effects of inorganic contamination on the elemental composition of samples of organisms can be estimated using interelement ratios and a mass balance for each element. To do this, the concentrations of Sc and the other elements of interest must be measured in the sample of organisms and in a separate sample of the contaminating material. Since most of the inorganic contamination of organisms results from inorganic material (sediment, etc.) in the alimentary canal of the organisms, samples of organisms and their excreted casts would be appropriate samples to analyze.

To correct for the effects of inorganic contamination, it must be assumed that for any element X with a concentration of C^X_{meas} in an organism (mass of element:mass of organism), the ratio of that portion of the total concentration contributed by contamination, C^X_{contm}, (mass of element:mass of organism) to the concentration measured in the excreted casts, C^X_{cast} (mass of element:mass of casts) is equal to the corresponding ratio for any element not assimilated by the organism. This ratio is given in Eq. (1).

$$\frac{C^X_{contm}}{C^X_{casts}} = \frac{C^{Sc}_{contm}}{C^{Sc}_{casts}} \qquad (1)$$

This approach also assumes that the ratios of elemental concentrations measured in the excreted casts are the same as those for the casts remaining in the organism.

The total mass of each element in the organism is the sum of the mass of that element in the organism and in the contaminate (unexcreted casts) (Eq. 2).

$$C^X_{meas}(M_{sample}) = C^X_{organism}(M_{sample}-M_{contm}) + C^X_{contm}(M_{sample}) \qquad (2)$$

where

M is the mass

Because Sc is not assimilated, the term C^{Sc}_{contm} (Eq. 1) is equal to C^{Sc}_{meas} (mass of Sc:mass of organism). The ratios of the Sc concentrations give the ratio of the mass of contaminate:the mass of the sample (Eq. 3).

$$\frac{M_{contm}}{M_{sample}} = \frac{C^{Sc}_{meas}}{C^{Sc}_{contm}} \quad (3)$$

Combining Eq. (1, 2, 3) yields Eq. (4), which gives the concentration of element X in the organism corrected for the effects of contamination.

$$C^{X}_{organism} = \frac{C^{X}_{meas} - C^{X}_{casts} C^{Sc}_{meas}/C^{Sc}_{cast}}{1 - C^{Sc}_{meas}/C^{Sc}_{cast}} \quad (4)$$

To determine the effectiveness of this procedure to correct for the effects of inorganic contamination and the seriousness of such contamination on the measured concentrations of elements in samples of organisms, *Asellus racovitzai* and their excreted casts were analyzed.

The concentations of selected elements in samples of casts collected from *Asellus* are given in Table 27. The concentrations of Zn (600 to 1,700 μg/g) are much higher than those normally found for sediments and organisms. This indicates that the detritus consumed by *Asellus* is greatly enriched in Zn. The concentrations of Se, Cr, and Ba are much higher in the samples from the ashpit drain (site BC) and Rocky Run Creek (site C) than in the samples from the other sites, providing strong evidence that these elements are being leached from fly ash, discharged into the drainage system of the ashpit, and ingested by *Asellus*. The concentrations of Fe and As are relatively high in the samples from the mint drain (site MD). This may be normal because this watercourse drains soils rich in organic matter, and the low redox potential of this water tends to dissolve Fe oxides and As associated with the Fe oxides.

The concentrations of REEs, Hf and Sc in *Asellus* are near zero after correction for inorganic contamination. The value for other elements, such as As, Br, Na, K, and Rb, are affected only slightly by inorganic contamination. The concentrations of Ba, Cr, and Se in *Asellus* are affected by the ash effluent more than those of any other element. The average concentrations of these elements plus Zn before and after correction for *Asellus* of different sizes and collection sites are given in Table 28. The concentrations of Zn and Se are affected only slightly by the correction, implying that almost all of these elements are from the body tissues of the organisms. The casts contribute only insignificant amounts of the total Zn and Se. However, significant amounts of Ba and Cr are contributed by the casts remaining in the analytical sample, especially for those samples affected by the effluent from the ashpit basin (site BC) as shown by differences in the original and corrected concentrations (Table 28).

The significance of the correction for Ba and Cr implies that high proportions of elements released from the ashpit are associated with solid detritus ingested by *Asellus*. However, calculations provide strong evidence

TABLE 27. CONCENTRATIONS (g/g) OF SELECTED ELEMENTS IN COMPOSITE SAMPLES OF CASTS FROM *ASELLUS RACOVITZAI*

Element	MD			BC		C
	1/13/78		2/28/78	2/1/78	3/1/78	1/20/78
	< 1 cm	> 1 cm	all	all	all	all
As	13 ± 4	10 ± 2	42 ± 9	25 ± 6	20 ± 5	14 ± 5
Ba	170 ± 40	220 ± 20	290 ± 50	8,200 ± 80	4,700 ± 200	1,300 ± 60
Cr	42 ± 2	61 ± 2	47 ± 2	240 ± 5	170 ± 7	240 ± 5
Fe	19,000 ± 300	18,000 ± 200	54,000 ± 600	13,000 ± 300	17,000 ± 600	28,000 ± 300
Sb	0.7 ± 0.2	0.5 ± 0.1	---	2.9 ± 0.4	1.4 ± 0.4	2.1 ± 0.3
Sc	2.3 ± 0.03	2.4 ± 0.02	2.4 ± 0.02	2.0 ± 0.03	3.9 ± 0.06	3.2 ± 0.03
Se	10 ± 1	10 ± 1	10 ± 1	170 ± 3	110 ± 5	130 ± 5
Zn	1,200 ± 30	1,200 ± 30	600 ± 20	760 ± 20	600 ± 20	1,700 ± 40

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[a] Analytical uncertainties represent one standard deviation based on counting statistics.

TABLE 28. CONCENTRATIONS (g/g) OF SELECTED ELEMENTS IN *ASELLUS RACOVITZAI* BEFORE AND AFTER CORRECTION FOR INORGANIC CONTAMINATION[a]

Element		MD						BC					
		1/13/78			2/28/78			2/1/78			3/1/78		
		<1 cm (3)[b]	1 cm (2)	>1 cm (2)	<1 cm (5)	1 cm (5)	>1 cm (8)	<1 cm (1)	1 cm (1)	>1 cm (2)	<1 cm (2)	1 cm (1)	>1 cm (2)
Ba	Original	22±4	---	---	25±4	20±3	27±9	120	132	120±15	280±150	150	190±7
	Corrected	---	---	---	19±3	14±4	23±8	53	29	34±21	200±160	61	65±30
Cr	Original	2.0±0.5	---	---	1.0±0.2	1.2±0.2	1.6±0.8	9.2	9.4	7.9±0.7	10±0.5	10	11±0.1
	Corrected	1.8±0.5	---	---	0.4±0.2	0.4±0.5	0.6±0.7	7.3	6.5	3.6±1.7	6.9±0.5	6.8	6.6±1.3
Se	Original	4.2±0.5	3.9±0.2	3.5±0.6	4.1±0.3	3.6±0.3	3.0±0.7	82	49	57±2	69±1	52	49±5
	Corrected	4.3±0.5	3.8±0.1	3.5±0.6	4.0±0.3	3.5±0.3	2.8±0.6	81	47	56±2	68±1	51	47±4
Zn	Original	83±8	82±5	86±6	83±6	79±7	74±12	84	75	68±3	76±2	70	81±7
	Corrected	78±5	73±6	79±6	74±11	67±19	62±15	78	66	61±4	65±3	60	66±3

[a] Analytical uncertainties represent one standard deviation based on counting statistics.

[b] Number of replicate samples.

that high concentrations of Ba and Cr as well as Se found in aquatic organisms affected by the ash effluent result from a high body burden of these elements--not from detritus in their intestinal tract.

Effect of Specimen Size on Elemental Concentrations

Organism size varied as a function of the collection site and time. The effect of the ash effluent on the concentrations of elements in organisms is determined by comparison of affected and control samples. Any changes in elemental concentrations that result from changes in the size of the organisms must be separated from the changes caused by the ash effluent.

Correlations between element concentrations and specimen size are summarized in Table 29. Correlations statistically significant at or beyond the 0.5 level were found for Ba, Br, Ca, Co, Cr, Fe, K, Mn, Na, Rb, Se, and Zn in at least one taxon. The correlations for *A. racovitzai*, Corixidae, and *Dineutus* spp. hold for data from specimens collected at all sampling sites and dates. However, the correlations for Odonata samples are specific for a particular site and date of collection.

TABLE 29. LEVELS OF SIGNIFICANCE FOR LINEAR CORRELATIONS OF ELEMENTAL CONCENTRATIONS AS A FUNCTION OF SPECIMEN SIZE FOR THE AQUATIC INVERTEBRATE TAXONS

Element	*Asellus racovitzai*	*Dineutus* spp.	Corixidae	Odonata
As	--	--		0.10
Ba	--[a]	--	0.05	--
Br	[a]	0.001[a]	0.001[a]	0.10
Ca	--	0.05[a]	--	
Co	--	0.01[a]	0.01[a]	0.05[a]
Cr	--	0.01[b]	0.05	0.05[a]
Fe	--	--	0.01	--
Hf	0.10[c]	--	--	--
Hg	0.10[ac]	--	--	--
K	0.05	0.01[a]	0.02[a]	0.02[a]
Mn	--	0.02[a]	0.001[a]	--
Na	0.10[a]	0.01[a]	0.001[a]	0.02[a]
Rb	--	0.10[a]	--	0.02[a]
Se	0.10[a]	--	0.001[a]	0.05[a]
Zn	--	0.01[a]	--	0.05[a]

[a] A parabolic curve fit is significant beyond the 0.05 level. The symbol-- means no significant correlation ($p > 0.10$).

[b] Only 1976 data from sites BC and RRL are included.

[c] Direct correlation; others are inverse.

The fact that the surface area:volume ratio is greatest for small organisms may influence concentrations and specimen size for several reasons. First, elements present in significant quantities on the organism surface, or associated in some manner with its exoskeleton, are expected to be present in relatively higher concentrations in smaller organisms.

Second, trace element uptake may take place by absorption through the exoskeleton. Little is known concerning the permeability of arthropod surfaces or the relative importance of element uptake through the alimentary canal compared with the organism's surface. Permeability studies on arthropods have traditionally been performed by measuring the rate of water movement out of the organism. This method is indirect, however, because it measures surface temperatures (Beament 1961a). For insects, the permeabilities from these studies can only be used in a qualitative manner as estimates of the rate of water intake, due to asymmetric permeability across the cuticle (Beament 1961b). Permeability among aquatic insects varies tremendously. In general, adult coleopterans (e.g. *Dineutus* spp.) and mature and immature hemipterans (e.g. Corixidae) are relatively impermeable; whereas dragonfly nymphs (Odonata) are relatively permeable (Beament 1961a). Differences in cuticle permeability may account partially for the observation that concentrations of As, Ba, Br, Ca, Cr, Eu, Fe, Hf, La, Rb, Sc, Se, and Sm are significantly higher in Odonata than in Corixidae and *Dineutus* spp.

Third, the amount of extracellular fluid decreases relative to intracellular fluid as the organism increases in size (Forbes 1968). Elements predominant in extracellular fluid would be more concentrated in small specimens. Concentrations of Br, Ca, and Na are higher outside the cell than inside, and concentrations of K are usually higher inside (Hughes 1972, Underwood 1971). Inverse correlations between concentrations of Br, Ca and Na and a direct correlation between K and organism size is expected. However, statistically significant inverse correlations ($p < 0.05$) were found between Na and K concentrations and *A. racovitzai*, Corixidae, *Dineutus* spp., and Odonata specimen size. Statistically significant inverse correlations were also found between concentrations of Br and Ca, and mean specimen size of Corixidae and *Dineutus* spp. This indicates that the relative distribution of elements between extra- and intracellular fluids plays a minor role in determining element concentrations in whole organisms.

Effects of the Ashpit Effluent on Concentrations of Elements in Aquatic Invertebrates

General Approach--

The general approach used to determine the effects of the effluent from the ashpit basin on the concentrations of elements in aquatic invertebrates was to compare the concentrations of elements in affected samples to those in control samples. The effects of organism size and inorganic contamination are considered when sufficient data are available. The organism found to be most suitable to meet the objectives of this study was *A. racovitzai*. This organism was abundant and good composite samples were collected at most sampling sites. Data collected on this species provides the best evidence of the effects of the ash effluent. The data for the other species are less comprehensive. However, all of the results obtained for the other species lead to the same conclusions as those for *Asellus*.

The data obtained for the *Asellus* samples collected between January and March 1978 provide the clearest evidence for the effects of the ash effluent. These samples are discussed first. Data for other species and for *Asellus* collected earlier are discussed afterwards, with emphasis on the elements found to be enriched in the 1978 collection of *Asellus*.

Asellus racovitzai--

The average concentrations of Ba, Cr, Se, and Zn in replicate, composite samples of *Asellus* are given in Table 28. Concentrations are given before and after correction for inorganic contamination for three different sizes of specimens. The data are the most suitable for determining the effects of the ash effluent. The effect on elemental concentrations resulting from a few weeks difference in time of collection is thought to be small. Fewer samples were available from the affected site (BC) because of the absence of suitable habitat in the man-made canal and maybe because of poorer water quality resulting from the soluble salts in the ashpit effluent.

Comparison of results from the control site (MD) to those from the affected site shows concentrations of Ba, Cr, and Se that are consistently and significantly higher in samples from the affected sites. The high concentrations of Ba, Cr, and Se in the affected samples do not result from the inclusion of inorganic material with high concentrations of these elements in the analytical sample, since the correction procedure (based on element ratios to Sc) subtracts this contribution. The corrected data indicate only the concentrations of these elements that are incorporated into tissues of the organisms. This distinction is important because elements ingested, but not absorbed, by the organism are thought to be less toxic than elements which are absorbed. Also, elements in the body tissues of prey organisms in predator-prey relationships are thought to pass more readily up the food chain than those elements which occur only as ingested material in the gut of the prey.

The concentrations of Se are 10 to 20 times greater in the affected samples than in the control samples. The measured concentrations are only slightly affected by correction. It is important to keep this in mind when examining the data available for other species, where insufficient data precludes making any correction for inorganic contamination. The concentrations of Se decrease with increasing size of the organism for control and affected samples.

Concentrations of Cr are generally < 1 μg/g in the control samples but in the affected samples concentrations of Cr are as high as 7 μg/g. Significant amounts of Cr in the analytical samples result from inorganic contamination, as shown by differences between measured and corrected concentrations. This also is true for Ba. Concentrations of Zn are the same for control and affected samples. Zinc was included in Table 28 because its behavior is similar to other transition elements with an ionic charge of +2. Of the elements studied, only Ba, Cr, and Se have higher concentrations in affected than control samples.

Barium in *Asellus racovitzai, Hyallela azteca*, and Odonata--

Concentrations of Ba in samples of *A. racovitzai, H. azteca*, and Odonata are significantly higher in samples collected in the ashpit drain on dates following start-up of the generating station. Correlations do not exist between Ba and organism size or Ba and other elements.

Concentrations of Ba in each species are summarized in Tables 30 through 33. Data are shown for those samples when controls and affected organisms were collected at the same time, thereby minimizing seasonal variability.

TABLE 30. CONCENTRATIONS (μg/g) OF Ba IN *ASELLUS RACOVITZAI*[a,b]

Site	Date of collection				
	10/22/74	9/26/75	10/16-17/75	1/23/76	2/16/76
A	33 ± 3	120 ± 10	165 ± 9	--[c]	--
B	37 ± 8	330 ± 30	200 ± 30	--	--
BC	--	--	129 ± 5	--	--
C	38 ± 7	--	199 ± 7	--	--
D	15 ± 4	--	--	700 ± 30[d] 420 ± 10[f]	390 ± 10[e]
Mint drain	--	--	21 ± 4	20 ± 3	43 ± 4[g] 25 ± 6[e]
Mean of ashpit drain	31 ± 11	225 ± 105	173 ± 34		--

[a] Each reported concentration is the result of analyzing a single composite sample.
[b] Analytical uncertainties represent one standard deviation based on counting statistics.
[c] -- indicates that no sample was analyzed.
[d] Composite of full-gutted specimens.
[e] Composite of female specimens.
[f] Composite of empty-gutted specimens.
[g] Composite of male specimens.

Table 30 shows Ba concentrations in *A. racovitzai*. The ashpit drain samples from 22 October 1974 were collected prior to start-up of the station and may be compared with samples collected on 16 and 17 October 1975. Ashpit drain samples collected on 16 and 17 October 1975 and 23 January, and 16 February 1976 may be compared with control samples from the mint drain. Student's T test was applied to estimate the probability that two independently collected samples are part of the same, normally distributed population. The 22 October 1974 ashpit drain samples (31 ± 11 μg/g Ba) are different at the 0.001 significance level from the 16 and 17 October 1975 ashpit drain samples (173 ± 34 μg/g Ba). Also, the 16 and 17 October 1975 and 16 February 1976 mint drain samples are lower than the ashpit drain samples at the 0.05 level of significance.

Tables 31 and 32 show Ba levels in samples of Odonata collected during fall and winter. For fall samples, specimens from site RRU serve as controls. These samples have lower Ba concentrations at the 0.01 significance level than do site BC samples collected at the same time. Because of higher standard deviations for site C samples, it cannot be shown that they are significantly different from RRU controls. For samples collected on 23 January 1976, the two mint drain specimens serve as controls. Concentrations of Ba are below detection limits in these specimens, they are significantly lower than site C specimens.

TABLE 31. CONCENTRATIONS (μg/g) OF Ba IN *LIBELLULA* SP. (ORDER:ODONATA) ON 7 OCTOBER 1976[a]

	Site RRU	Site C	Site BC
	15 ± 4	13 ± 4	32 ± 6
	21 ± 5	25 ± 6	34 ± 6
	< 21	26 ± 4	36 ± 7
Mean	18 ± 3	21 ± 7	34 ± 2

[a] Analytical uncertainties represent one standard deviation based on counting statistics.

TABLE 32. CONCENTRATIONS (μg/g) OF Ba IN SAMPLES OF LIBELLULIDAE (FAMILY, ORDER:ODONATA) ON 23 JANUARY 1976[a]

Mint drain	Site C	
< 12	14 ± 4	
< 15	25 ± 5	
--	28 ± 6	
Mean	<15	22 ± 7

[a] Analytical uncertainties represent one standard deviation based on counting statistics.

Table 33 shows Ba concentrations in *H. azteca* collected from the ashpit drain before and after start-up of the plant. Concentrations from affected sites are higher than control sites.

TABLE 33. CONCENTRATIONS (μg/g) OF Ba IN *HYALLELA AZTECA*[a,b]

Site	Date of collection 22 October 1974 Control	 16 October 1975 Affected
A	40 ± 10	26 ± 3
		71 ± 7
B	15 ± 4	200 ± 10
C	18 ± 5	---
D	< 20	---

[a] Each reported concentration is the result of analyzing a single composite sample.

[b] Analytical uncertainties represent one standard deviation based on counting statistics.

Large quantities of $BaSO_4$ from the ashpit effluent precipitate in the ashpit drain above and below its confluence with the mint drain. The precipitate can be seen on bottom sediments throughout the ashpit drain and it decreases in abundance with distance downstream. The high concentrations of Ba in *A. racovitzai* and *H. azteca* from sites affected by the ash effluent may result in part from $BaSO_4$ precipitated onto organisms which are then ingested. Comparison of full- and empty-gutted *A. racovitzai* indicates that Ba in sediment is a source of the element, at least for this detritus feeder. The full-gutted composite sample had 700 ± 30 μg/g Ba, while "empty-gutted" specimens had 420 ± 10 μg/g Ba. Examination of organism surfaces with a scanning electron microscope equipped with x-ray fluorescence did not detect Ba. The significance of the concentrations of Ba measured in the analytical samples for estimating the ingested Ba in the gut, also is shown in Table 28. Thus, $BaSO_4$ precipitated in ash effluent is a source of Ba ingested by detritus feeders. The water also is saturated with $BaSO_4$ and dissolved Ba is another likely source. Organisms sampled in the drainge system of the ashpit have higher concentrations of Ba than control samples.

Chromium in *Asellus racovitzai* and Odonata--

Concentrations of Cr in samples of *A. racovitzai* and Odonata are significantly higher in samples collected from the ashpit drain after start-up of the plant than in earlier control samples or in control samples from Rocky Run Creek and the mint drain. Correlations did not exist between Cr and organism size or Cr and other elements.

Concentrations of Cr in *A. racovitzai* are summarized in Table 34. Control samples collected on 22 October 1974 may be compared with affected samples collected on 16 and 17 October 1975. The Cr concentration in the former samples is 2.3 ± 0.7 μg/g and in the latter is 12 ± 3 μg/g (significantly different at the 0.001 level). Affected samples collected on 16 and 17 October 1975 and 23 January and 16 February 1976 may be compared with control samples from the mint drain at corresponding times. Control specimens have less Cr ($p \leq 0.05$) than specimens collected from affected sites.

TABLE 34. CONCENTRATIONS (μg/g) OF Cr IN *ASELLUS RACOVITZAI*[a,b]

	Date of collection				
Site	10/22/74	9/26/75	10/16-17/75	1/23/76	2/16/75
A	2.6 ± 0.1	4.0 ± 0.5	9.6 ± 0.4		
B	2.9 ± 0.4	11 ± 0.4	11 ± 0.3		
BC	--[c]		12 ± 0.8		
C	2.1 ± 0.3	--	16 ± 0.4		
D	1.4 ± 0.3	--	--	15 ± 1[d] 16 ± 0.5[f]	13 ± 1[e]
Mint drain	--	--	1.4 ± 0.2	1.8 ± 0.1	2.4 ± 0.2[g] 1.4 ± 0.3[f]
Mean	2.3 ± 0.7	8 ± 4	12 ± 3	15 ± 0.6	--

[a] Each reported concentration is the result of analyzing a single composite sample.

[b] Analytical uncertainties represent one standard deviation based on counting statistics.

[c] --indicates that no sample was analyzed.

[d] Composite of full-gutted specimens.

[e] Composite of female specimens.

[f] Composite of empty-gutted specimens.

[g] Composite of male specimens.

Tables 35 and 36 give the Cr concentrations in Odonata specimens collected in fall and winter from control sites and sites affected by ash effluent. All control specimens have lower Cr concentrations ($P \leq 0.01$). Insufficient data is available to examine relationships of Cr in Corixidae.

Some Cr results from inorganic material in the guts of the organisms (Table 28). However, corrected data show that Cr is taken up by the organisms.

TABLE 35. CONCENTRATIONS ($\mu g/g$) OF Cr IN *LIBELLULA* SP. ON 7 OCTOBER 1976[a]

	Site RRU	Site C	Site BC
	4.1 ± 0.2	10 ± 0.3	14 ± 0.3
	5.7 ± 0.4	13 ± 0.5	12 ± 0.4
	5.0 ± 0.3	13 ± 0.3	13 ± 0.5
Mean	4.9 ± 0.8	12 ± 2	13 ± 1

[a] Analytical uncertainties represent one standard deviation based on counting statistics.

TABLE 36. CONCENTRATIONS ($\mu g/g$) OF Cr IN LIBELLULIDAE ON 23 JANUARY 1976[a]

	Mint drain	Site C
	0.9 ± 0.2	11 ± 0.6
	1.9 ± 0.5	8.2 ± 0.3
		9.0 ± 0.5
Mean	1.4 ± 0.5	10 ± 2

[a] Analytical uncertainties represent one standard deviation based on counting statistics.

Selenium in *Asellus racovitzai* and Odonata--

Concentrations of Se in specimens exposed to the ash effluent are higher than in control specimens ($p \leq 0.01$) when data for all Odonata are combined. To show that this difference is not due to sampling bias related to season or taxonomic group, concentrations of Se in specimens collected from affected and control sites on the same dates are presented in Tables 37 and 38. The Se contents of larvae of *Libellula* sp. collected from sites BC and C on 7 October 1976 are not different at the 0.05 significance level (4.0 ± 0.4 and 3.0 ± 0.7 $\mu g/g$, respectively). The Se concentrations for specimens from the two sites (3.5 ± 0.7 $\mu g/g$) are higher than control samples from site RRU at the 0.05 level of signficance. Similarly, Se concentrations in specimens of *Sympetrum* sp. from site C are higher than those in control samples collected from the mint drain on the same date ($p \leq 0.02$).

TABLE 37. CONCENTRATIONS ($\mu g/g$) OF Se IN *LIBELLULA* SP. ON 7 OCTOBER 1976[a]

	Site RRL[b]	Site RRU	Site C	Site BC
	2.9 ± 0.4	2.2 ± 0.3	3.2 ± 0.6	3.5 ± 0.5
	3.3 ± 0.6	2.3 ± 0.3	2.3 ± 0.3	4.2 ± 0.6
	3.4 ± 0.6	2.3 ± 0.3	3.6 ± 0.7	4.2 ± 0.8
Mean	3.2 ± 0.3	2.3 ± 0.6	3.0 ± 0.7	4.1 ± 0.4

[a] Analytical uncertainties represent one standard deviation based on counting statistics.

[b] The specimens from site RRL are *Tetragoneuria* sp.

TABLE 38. CONCENTRATIONS ($\mu g/g$) OF Se IN *SYMPETRUM* SP. ON 23 JANUARY 1976[a]

	Mint drain	Site C
	1.9 ± 0.4	2.8 ± 0.3
	2.2 ± 0.2	2.9 ± 0.6
	2.7 ± 0.2	
Mean	2.1 ± 0.2	2.8 ± 0.1

[a] Analytical uncertainties represent one standard deviation based on counting statistics.

Selenium concentrations in the *Tetragoneuria* sp. collected from site RRL on 7 October 1976 are not significantly different from the *Libellula* sp. collected from site C on the same date, but are higher (0.01 significance level) than *Libellula* sp. collected from site RRU on the same date (Table 37). Because site RRL is downstream from the confluence of the ashpit drain and Rocky Run Creek, the organisms collected may be affected by the ash effluent. This would account for the similarity in Se concentrations between Odonata specimens collected from the ashpit drain and site RRL. However, the validity of comparing Se concentrations between Odonata specimens of different families or even genera has not been established. Differences in Odonata Se concentrations between specimens collected at affected and control sites are relatively small and could be due to natural, inter-population variability.

The mean Se concentrations for specimens collected from site C on 7 October and 23 January 1976 are not significantly different. Hence, there may be no significant seasonal or inter-family variations in Se concentrations of Libellulidae.

A significant correlation exists between Se concentration and Odonata specimen size. The correlations are unique for specimens of the same genus collected at different sampling sites at different times (Figure 15). The differences in Se concentrations between specimens exposed to the ashpit effluent and control specimens cannot be attributed to differences in specimen size, but could be due to natural, inter-population variability.

Concentrations of Se in Libellulidae larvae from a farm pond polluted with fly ash were found to be significantly higher than in larvae collected from a control pond (Gutenmann et al. 1976). The mean Se concentrations reported for the affected and control specimens--4.1 and 1.5 μg/g--are similar to those obtained for affected and control specimens in this study.

Concentrations of Se in affected and control samples of *A. racovitzai* collected on the same date are presented in Table 39. High standard deviations prevent detection of statistically significant differences between samples exposed to the ash effluent and control samples. However, mean Se concentrations of all samples exposed to ash effluent are higher than controls. Mean Se concentration in the ashpit drain control samples collected on 22 October 1974 is 4.3 ± 0.5 μg/g, which is lower than the 7 ± 2 μg/g for the samples collected from the same sites approximately 1 yr later. Selenium concentrations are higher in the ashpit drain samples collected in October 1975, January and February 1976 than in the mint drain control samples collected on the same dates. The Se data for *Asellus* given in Table 28 show that the affected samples have higher concentrations of Se than do control samples.

TABLE 39. CONCENTRATIONS (μg/g) OF Se IN *ASELLUS RACOVITZAI*[a,b]

	Date of collection				
Site	10/22/74	9/26/75	10/16-17/75	1/23/76	2/16/76
A	4.1 ± 0.4	5.1 ± 0.9	10 ± 2	--[c]	--
B	4.9 ± 0.8	6 ± 1	5.5 ± 0.9	--	--
BC	--	--	6.9 ± 0.8	--	--
C	3.7 ± 0.6	--	5.5 ± 0.9	--	--
D	4.6 ± 0.8	--	--	4.7 ± 0.7[d] 5.9 ± 0.5[f]	5.7 ± 0.9[e]
Mint drain	--	--	5.6 ± 0.9	3.4 ± 0.4	2.6 ± 0.2[g] 3.4 ± 0.3[e]
Mean of ash-pit drain	4.3 ± 0.5		7 ± 2		

[a] Each concentration is the result of analyzing one composite sample.
[b] Analytical uncertainties represent one standard deviation based on counting statistics.
[c] --indicates that no sample was analyzed.
[d] Composite of empty-gutted specimens.
[e] Composite of female specimens.
[f] Composite of empty-gutted specimens.
[g] Composite of male specimens.

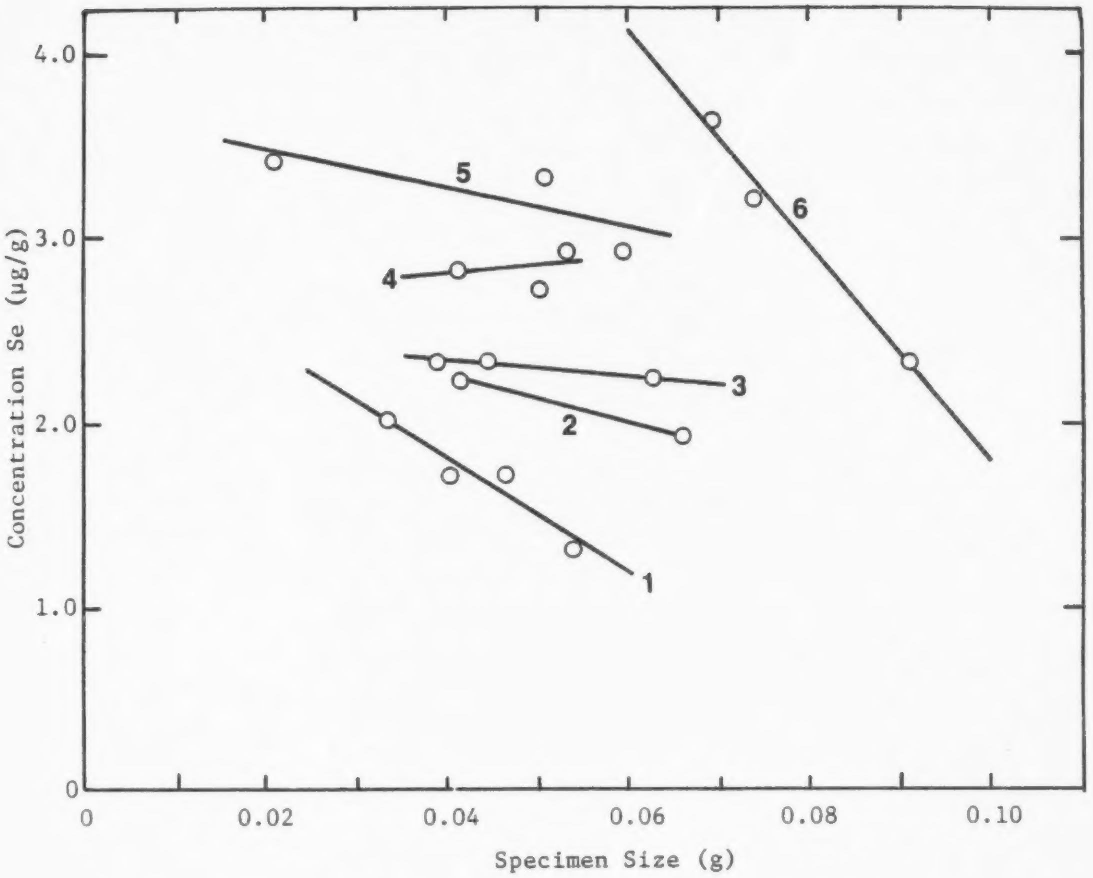


Figure 15. Concentration of Se as a function of specimen size for Odanata.
Line 1: Samples 010-013 (controls)
Line 2: Samples 08-09 (controls)
Line 3: Samples 019-021 (controls)
Line 4: Samples 05-07 (affected)
Line 5: Samples 016-018 (?)
Line 6: Samples 025-027 (affected)
Only data from the analysis of single specimen samples are plotted, with the exception of one data point on Line 5. This latter sample is composed of two specimens of approximately the same size.

Antimony in *Asellus racovitzai, Hyallela azteca, Gammarus* sp. and Corixidae--

Concentration of Sb could not be correlated with specimen size. Concentrations of Sb are significantly higher in *A. racovitzai* and Odonata specimens exposed to the ash effluent. No evidence exists to suggest that Sb concentrations in *H. azteca, Gammarus* sp., or Corixidae specimens are dependent on exposure to the effluent.

Concentrations of Sb in *A. racovitzai*, for which affected and control samples were collected on the same date, are presented in Table 40. Except for the mint drain sample collected on 23 January 1976 (0.0014 ± 0.0003 μg/g) and the site C sample collected on 22 October 1974 (0.06 ± 0.02 μg/g), Sb concentrations were below detection limits in the control samples. Mean Sb concentrations in samples collected from the ashpit drain on 26 September 1975, 16-17 October 1975, and 23 January 1976 were readily detectable at 0.15 ± 0.03, 0.16 ± 0.06, and 0.14 ± 0.05 μg/g.

TABLE 40. CONCENTRATIONS (μg/g) OF Sb IN *ASELLUS RACOVITZAI*[a,b]

	Date of collection				
Site	10/22/74	9/26/75	10/16-17/75	1/23/76	2/16/76
A	< 0.04	0.12 ± 0.03	0.25 ± 0.03		
B	< 0.03	0.17 ± 0.04	0.12 ± 0.02		
BC	--[c]	--	0.12 ± 0.02		
C	0.06 ± 0.02	--	0.14 ± 0.02		
D	< 0.05	--	--	0.18 ± 0.004[d]	0.06 ± 0.02[e] 0.09 ± 0.02[f]
Mint drain	--	--	< 0.06	0.0014 ± 0.0003	< 0.02[e] < 0.02[g]
Mean of ash-pit drain		0.15 ± 0.03	0.16 ± 0.06	0.14 ± 0.05	

[a] Each concentration is the result of analyzing one composite sample.

[b] Analytical uncertainties represent one standard deviation based on counting statistics.

[c] --indicates that no sample was analyzed.

[d] Composite of empty-gutted specimens.

[e] Composite of female specimens.

[f] Composite of empty-gutted specimens.

[g] Composite of male specimens.

The concentration of Sb in the composite sample consisting of "full-gutted" specimens collected from site D on 23 January 1976 is approximately twice that of "empty-gutted" specimens (0.18 ± 0.004 and 0.09 ± 0.02 μg/g, respectively). This indicates that the gut contents affect significantly Sb concentrations of organisms. Body burdens of Sb cannot be determined. Application of the correction procedure provided concentrations of Sb near zero. Thus, the high concentrations of Sb in the affected samples result from materials accumulated in the gut.

Concentrations of Sb in Odonata specimens are presented in Tables 41 and 42. Antimony was not detected in control specimens. Mean Sb concentrations in *Libellula* sp. collected from sites C and BC on 7 October 1976 are 0.14 ± 0.04 and 0.21 ± 0.03 μg/g. Mean Sb concentration for the three specimens of *Sympetrum* sp. collected from site C on 23 January 1976 (0.13 ± 0.005 μg/g) is essentially the same as that found for *Libellula* sp. collected at the same site on 7 October 1976. This would indicate that little or no variation occurs in Sb concentrations for Libellulidae due to seasonal or genus differences.

TABLE 41. CONCENTRATIONS (μg/g) OF Sb IN *LIBELLULA* SP. ON 7 OCTOBER 1976[a]

	Site RRU	Site C	Site BC
	< 0.03	0.11 ± 0.02	0.24 ± 0.03
	< 0.03	0.19 ± 0.04	0.20 ± 0.03
	< 0.03	0.12 ± 0.02	0.18 ± 0.02
Mean		0.14 ± 0.04	0.21 ± 0.03

[a] Analytical uncertainties represent one standard deviation based on counting statistics.

TABLE 42. CONCENTRATIONS (μg/g) OF Sb IN *SYPETRUM* SP. ON 23 JANUARY 1976[a]

	Mint drain	Site C
	< 0.17	0.14 ± 0.003
	< 0.03	0.14 ± 0.004
		0.13 ± 0.004
Mean		0.13 ± 0.005

[a] Analytical uncertainties represent one standard deviation based on counting statistics.

Suitability of Organisms Used in This Study to Monitor Ecosystem Fluxes of Elements

The characteristics that make an organism suitable for analysis in a study investigating the impact of elements on aquatic invertebrates were identified. To be useful as an indicator of ecosystem trace element fluxes, an organism must:

1) Be amenable to collection and analysis;
2) Be distributed widely throughout the study region;
3) Have been present at the site of collection long enough to reflect trace element conditions at the site;
4) Be relatively common to the habitat;
5) Be able to tolerate a wide enough range in water quality so that the organism is not killed, except under conditions of great stress;
6) Have sufficiently high concentrations of trace elements that can be correlated with environmental conditions;
7) Have sufficiently high concentrations of trace elements to give small sample standard deviation.

All arthropod taxons used satisfy above requirements 1 and 2. *Dineutus* spp. are very mobile and do not meet requirement 3. Requirements 4 and 5 are met by *A. racovitzai*, Corixidae, and Odonata. Insufficient data exist to evaluate the *Dineutus* spp., *Gammarus* sp., and *H. azteca* with respect to habitat distribution or tolerance to the range of water quality encountered at the ashpit drain and control sites. Because they were not found in the ashpit drain after 1975, *Gammarus* sp. and *H. azteca* may be less tolerant of the conditions in the ashpit drain than *A. racovitzai*, Corixidae and Odonata.

Corixidae and *H. azteca* do not satisfy requirement 6. Chromium, Sb, and Se were not detected in *H. azteca*, but *A. racovitzai* and Odonata, collected simultaneously at the same sites, contain these elements. Concentrations of Ba, Cr, Se, and Sb were undetected, or were significantly lower in Corixidae than in *A. racovitzai* or Odonata collected at the same site on the same date. No significant differences were found in elemental concentrations between exposed and control specimens of Corixidae. The ability of an organism to fulfill requirement 7 varies with each element and with the environmental conditions which affect its uptake. The most useful organisms for this type of survey are *A. racovitzai* and Odonata.

Effect of Ashpit Effluent on Elemental Concentrations in Frogs

Variables, seeming to affect the elemental concentrations in frogs (*Rana pipiens*), include type of tissue analyzed and dates and locations of collection. No evidence was found to suggest that sex or specimen size (length) affects elemental concentrations. Concentrations of As, Ce, Hf, La, Lu, Nd, Sm, Tb, Th, U, and Yb were below detection limits in all samples. Insofar as these elements are detected in a number of invertebrate samples collected at the same sites at the same time, attempts to monitor aquatic systems for these elements by analysis of frogs appear to be impractical.

Conclusions about the effects of power plant operation on elemental concentrations in frogs cannot be made with existing data. The control population consists entirely of specimens collected on one day in November 1974 preceding the start-up of the station. The test population consists entirely of specimens collected on one day after start-up in August 1975. In the absence of data showing how elemental concentrations change on a seasonal or daily basis, clarifications for observed differences cannot be made. Many reasons exist for suspecting that elemental concentrations vary naturally with time for a given location. For instance, concentrations of C, N, and P vary considerably with reproductive cycles, seasons, and availability of food in mollusks (Russell-Hunter 1970). Concentrations of Cd, Cr, Hg, Pb, and Zn in aquatic invertebrates are highest in the summer and early fall; seasonal variation in elemental concentrations in river water also were reported (Weiss et al. 1972). It seems reasonable to expect that essential (and perhaps non-essential) trace elements also vary in concentration in vertebrates. Examination of gut contents during dissection revealed that frogs collected in August were feeding more regularly than those collected in November. The diet of frogs collected in August consisted primarily of prey of terrestrial origin (grasshoppers, flies, caterpillars); frogs collected in November were feeding solely on prey of aquatic origin.

Antimony--

Antimony was only detected in the muscle sample collected at site D in November 1974 (0.017 ± 0.005 μg/g). It was not detected in skin samples, but was detected in all liver samples. The number of liver samples is insufficient to evaluate variability due to time, site, sex, or size. Concentrations of Sb in liver are higher for samples collected in August 1975 than in November 1974 at a given site, but only at the 0.1 significance level. Because specimens collected at the sampling site most affected by ash effluent (site D; composite of frogs c and d) had an Sb concentration 50% higher than any other sample analyzed, further investigations may be warranted.

Barium--

The highest concentrations of Ba in frog tissues occur in the skin. Skin samples have concentrations ranging from 34 ± 5 to 45 ± 5 and from 52 ± 5 to 80 ± 6 μg/g for 1974 and 1975. Mean concentrations for the 1974 and 1975 samples are 39 ± 7 and 66 ± 8. Because the values are means of only two samples, standard deviations cannot be determined. The uncertainty reported above was calculated by determining the square root of the sum of the squares of each sample's analytical uncertainty. No statistically significant difference was found in Ba concentrations in the skin samples between sampling dates ($p = 0.2$). High variability accounts for the inability to show a statistically significant difference. All four skin samples are from frogs collected at site D, the sampling site closest to the ash basin and, as of August 1975, the site with the largest amount of precipitated $BaSO_4$.

Barium in liver tissues seems to be as variable as in skin tissue. The four 1974 samples ranged in concentration from 11 ± 2 to 24 ± 2 μg/g. If the variables affecting Ba concentrations in frog tissues were homogeneous for control samples, then the 1974 samples could be viewed as a single population with a mean Ba concentration of liver of 16 ± 9 μg/g. The sample collected from site A in August 1975, with 15 ± 3 μg/g Ba in liver, is not significantly different from the 1974 site A sample and the 1974 mean. The level of 51 ± 2 μg/g for the 1975 sample from site D, however, is considerably higher than the levels for the two 1974 site D samples (11 ± 2 and 24 ± 2 μg/g). Also, the liver Ba level in the site D 1975 sample exceeds the mean of all 1974 samples by more than three standard deviations and is higher than the mean level of the 1974 samples ($p \leq 0.02$). The high Ba concentration in the 1975 site D sample may be due to the high Ba levels found at that sampling site.

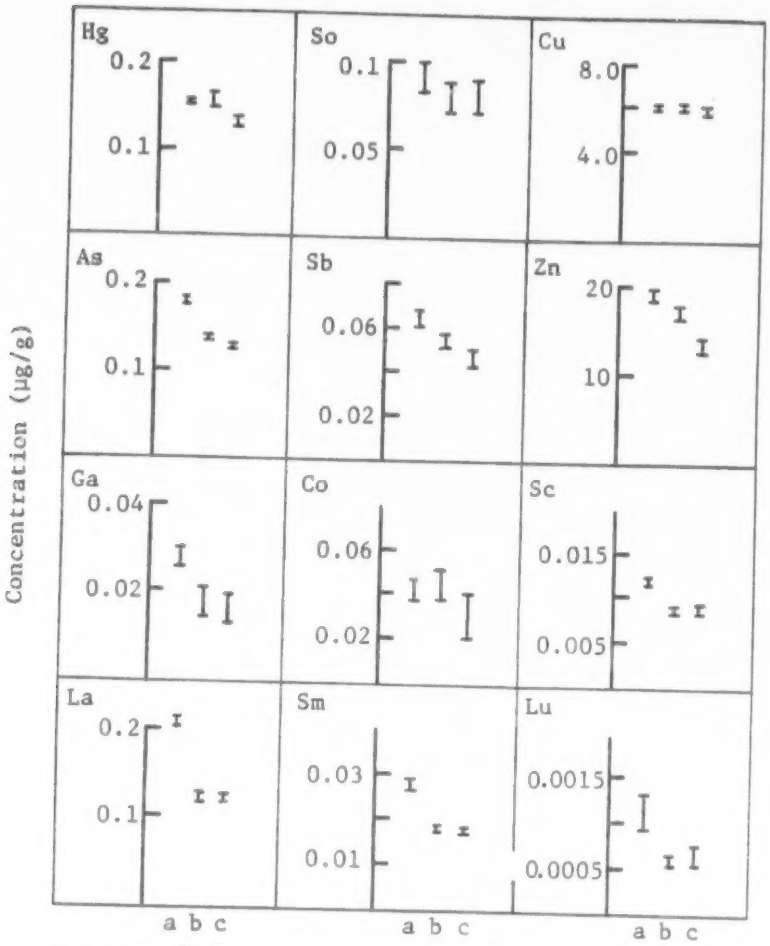
In summary, data on frogs are too limited to draw any conclusions. Concentrations of Ba in frog skin appear to be higher for the affected samples than control samples.

OAK LEAVES

Effects of Washing

The effects of washing on concentrations of selected elements in oak leaves are shown in Figure 16. The concentration of Cu--an essential nutrient--is not appreciably affected by washing. Washing reduces the concentration of elements contained in relatively high amounts in inorganic material and dust by 30 to 40%. No discernable differences exist between washing with water and HCl and water. Other essential elements display different patterns. Cobalt is unaffected by washing with water but may be lowered slightly by acid washing. Selenium, which is toxic at high levels, but essential in trace amounts, shows no significant decrease with washing. Of the potentially toxic elements, As and Sb are reduced by a water wash; the reduction is slightly greater with an acid wash. Mercury seems unaffected by washing with water, but is lowered slightly by acid washing.

Elements that are indicators of surface contamination by inorganic material--Ga, Sc, La, Sm and Lu--show that washing with water is just as effective as washing with 0.1 *N* HCl in removing such contamination. The fact that Hg, Zn, Sb, and possibly As and Co seem to be reduced more by washing with acid than with water suggests that this further reduction may be due to leaching of elements from the leaves. Washing with water appears to be as effective as an acid wash in removing inorganic contamination, a single wash with water reduces leaching of some elements from the leaves. A water wash has the additional advantage that no contaminants are added by washing. Washing the leaves with a detergent solution may remove additional material but this will contaminate the samples with P and S.



a = unwashed

b = washed three times with distilled water

c = washed once with 0.1*N* HCl, then twice with distilled water

Figure 16. Trace element concentrations in white oak leaves.

Bioaccumulation of Eu, Hf, Sc, and Tb

The concentrations of Eu, Hf, Sc and Tb in oak leaves are given in Table 43. The uncertainties are based on counting statistics. Only two seedlings survived in pots 2 and 3. All of the concentrations of Hf were below the limit of detection.

The concentration of Eu and Tb in oak leaves from the bioaccumulation experiment are much greater than those of natural samples. This is expected because concentrations of soluble Eu and Tb added to the soil are much greater than levels found in natural soils. In contrast to Eu and Tb, concentrations of Sc in oak leaves are only a few ng/g, which is about the same as that for natural samples. The Sc is taken up only in small amounts even when it is applied initially in a soluble form. This implies that concentrations of Sc > 5 ng/g in natural oak leaves must result from inorganic contamination. The actual cutoff level is probably much < 5 ng/g because of the high concentration of soluble Sc used in the bioaccumulation experiment. Thus, Sc in oak leaves is probably the best indicator of inorganic contamination.

TABLE 43. BIOACCUMULATION (μg/g) OF Eu, Hf, Sc, AND Tb BY LEAVES OF WHITE OAK SEEDLINGS

Pot and seedling	Eu	Hf	Sc	Tb	Sample weight (g)
1A	0.37	< 0.23	0.0077	0.39	0.23854
1B	0.27	< 0.30	< 0.0039	0.35	0.33348
1C	0.30	< 0.17	< 0.0041	0.32	0.74831
2A	0.28	< 0.25	0.0105	0.36	1.09245
2B	0.36	< 0.093	< 0.0022	0.38	1.23133
3A	0.32	< 0.19	0.0057	0.34	0.92942
3B	0.56	< 0.18	0.0072	0.62	0.96643
5A	0.44	< 0.095	< 0.0023	0.29	1.06998
5B	0.22	< 0.23	0.0031	0.30	0.99647
5C	0.35	< 0.15	0.0063	0.45	1.24788
One standard deviation from analytical uncertainty (%)	1	--	30	10	

If desired, the ratio of the concentration of each element to that of Sc can be used to correct the concentration of each element in the leaves for inorganic contamination, in a manner previously outlined for aquatic invertebrates. In the case of oak leaves, the elemental composition in the aerosolic dust from the collection site nearest each oak leaf site can be used as an approximation of the composition of the dust on the oak leaves.

Sampling Errors

The average concentrations of elements and the standard deviation from the mean for the 15 samples of washed white and black oak leaves obtained at sites D12 and FW36 are presented in Table 44. Comparison of the standard deviation from the mean and the analytical uncertainty (one standard deviation based on counting statistics) for each element shows that they are similar. This implies that the sampling error is about the same as the analytical uncertainty and that analysis of a single composite sample gives accurate and reproducible values for elemental composition of leaves.

Aerosolic Dust on Oak Leaves

Samples of black oak leaves collected in 1976 from site W5 (samples not washed after collection) were examined by electron microscopy to determine the abundance of fly ash particles and aerosolic dust on the surface of the leaves. Examples of the morphology of the upper surfaces of these leaves and the location of air particulates on the leaf surfaces can be seen in Figure 17. Similar information concerning the lower sides of the leaves is shown in Figure 18. The data for the leaf surfaces is divided into veinal and non-veinal areas and is presented in Table 45. Table 46 shows the surface compositions for 100 randomly selected fly ash particles from upper and lower leaf surfaces for each month during 1976.

Examination of the upper and lower surfaces of black oak (*Quercus velutina*) leaves indicates that the major site of collection of ash on the oak leaves is along the veins. Here a number of small, crenulate folds occur in which the particles can be entrapped. As the leaves continue to grow, the waxy layer found on the surface of the black oak leaves in some cases appears to engulf, or begins to engulf, some of these foreign particles.

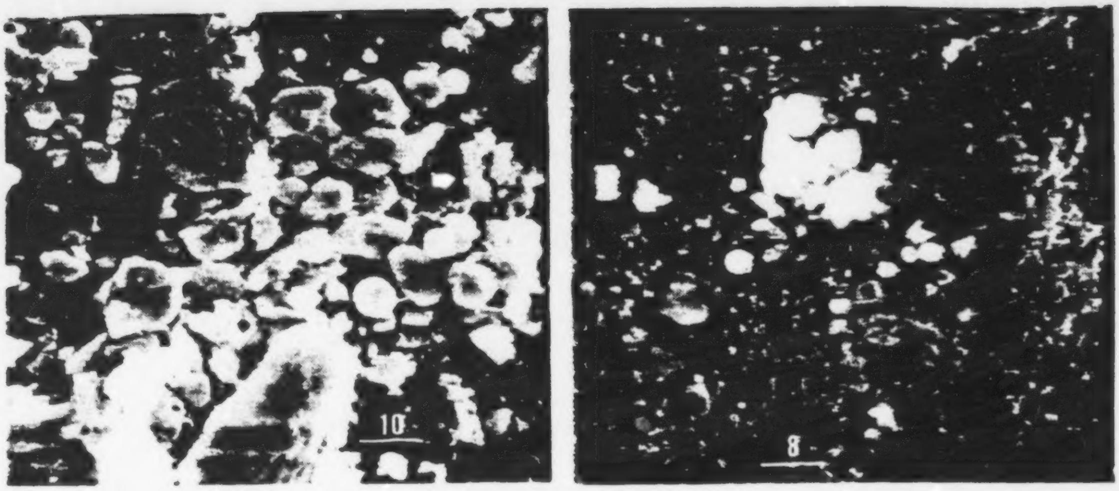
In Figure 18 the stomata, which occur only on the lower sides of the leaves in black oak, generally seem to be free of ash particles. This is especially true for samples collected when the leaves were young, such as in May, when the lower surfaces had irregular shapes. As the leaves mature, the density of stomatal openings decreases from a high of 21 openings/2,800 μm^2 in May to an average of 13 in August, September, and November. This trend is shown in Figure 19. It is important to note that very little ash appears to be entrapped or on the stomata guard cells. It is uncertain why these cells close, but it may be in response to ash particles coming in contact with them, thus preventing the entry of these particles into the interior of the leaf. It may also be a case of vapor being released through the stomatal openings, thereby pushing any incoming particles away from the stomata themselves.

The flux of the ash collected on the leaves for site W5 is shown in Table 46. Each number in the table is an average of 20 measured areas, each consisting of 2,800 m^2. The data for the leaf surfaces is divided into

TABLE 44. AVERAGE ELEMENTAL COMPOSITION OF 15 SAMPLES OF BLACK AND WHITE OAK LEAVES

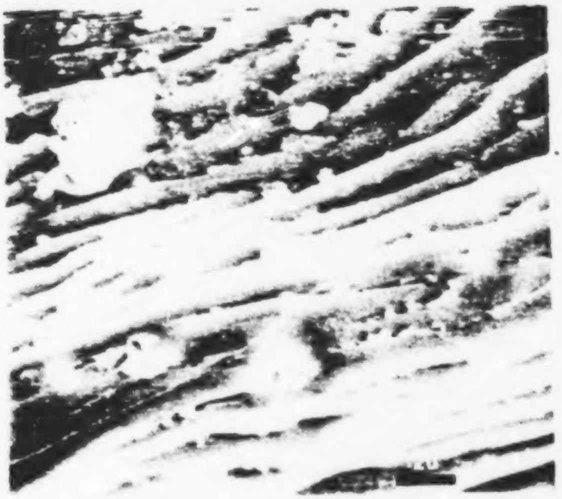
	Black Oak			White Oak			
Element	Number of measurements	Mean concentration (μg/g)	Standard deviation (%)	Number of measurements	Mean concentration (μg/g)	Standard deviation (%)	Analytical uncertainty[a] (%)
As	10	0.03	75	--	--	--	10
Ba	15	83	4.5	15	110	4.8	4
Br	15	2.3	6.2	15	5.7	3.3	3
Ca	15	83,000	3.2	15	100,000	5.8	20
Cd	10	0.2	74	--	--	--	25
Ce	5	0.1	150	15	0.36	12	2
Co	15	0.017	10	15	0.029	13	4
Cr	11	0.2	79	14	0.3	56	3
Cs	15	0.054	4.3	15	0.25	5.9	7
Cu	10	5.0	75	--	--	--	3
Eu	15	0.008	8.8	15	0.010	14	5
Fe	15	55	8.2	15	85.0	21	3
Hf	3	0.008	250	3	0.02	240	10
Hg	10	0.04	75	--	--	--	5
K	15	9,000	3.5	15	8,300	4.2	15
La	15	0.18	6.3	15	0.25	9.9	5
Lu	6	0.001	140	--	--	--	5
Mn	15	1,700	5.8	15	2,100	6.8	3
N	15	22,000	6.9	15	23,000	3.5	--
Na	15	66,000	1.2	15	98,000	1.5	2
P	15	1,800	2.8	14	2,300	3.0	--
Rb	15	14	5.4	15	36	4.2	10
S	15	1,600	2.5	14	1,600	2.8	--
Sb	13	0.009	49	15	0.020	19	20
Sc	15	0.007	14	15	0.012	14	--
Se	--	--	--	3	0.02	230	15
Sm	15	0.030	8.3	15	0.033	12	10
Tb	15	0.0053	13	10	0.006	76	20
Th	4	0.01	200	7	0.02	230	50
Yb	12	0.008	50	5	0.01	110	10
Zn	15	34	5.1	15	15	3.7	5

[a] One standard deviation.



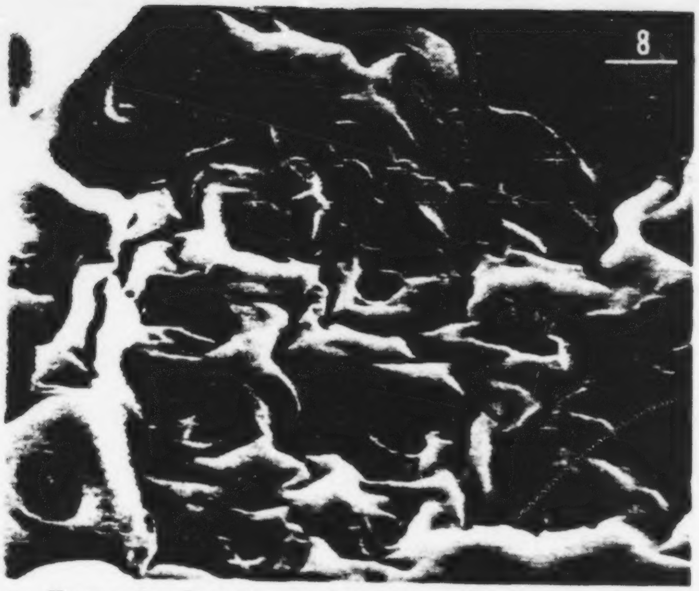
a. Aerosolic dust sample from site P24.

b. Aerosolic dust particles concentrated in depressions on upper leaf surface.

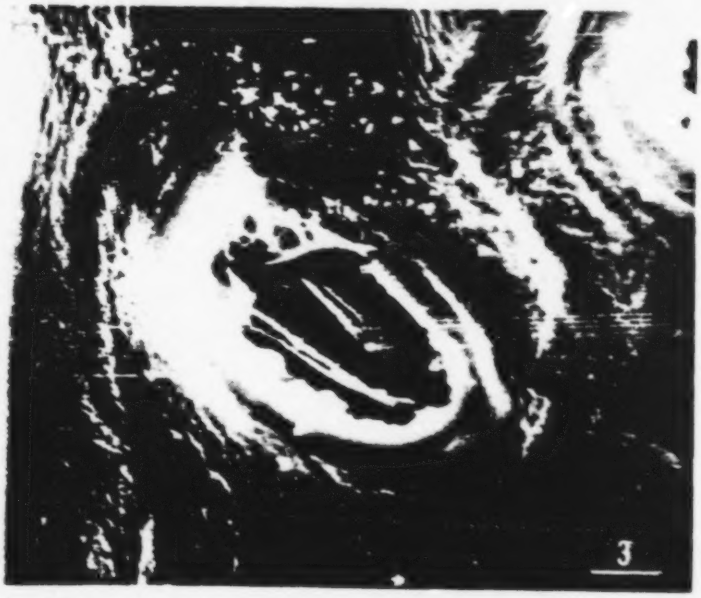


c. Aerosolic particles concentrated on the upper leaf veins.

Figure 17. Electron photomicrographs of aerosolic particles collected in the dust bucket and on the upper surfaces of black oak leaves. The scale in µm is given by the bar. The round spherical particles are fly ash.



a. Young leaf collected in May showing a very irregular surface free of aerosolic dust.



b. Mature leaf collected in August with numerous tiny aerosolic particles on it.

Figure 18. Electron photomicrographs of aerosolic particles collected on the lower surfaces of black oak leaves from site W5 during 1976. The round, spherical particles are fly ash. The scale is given by the bar in μm.

TABLE 45. DIFFERENTIATION OF FLY ASH COLLECTED ON BLACK OAK LEAVES AT SITE W5 DURING 1976

Collection date	Leaf surface	Columbia fly ash (%)	Non-Columbia fly ash (%)	Fly ash of uncertain affinities (%)
05-20	Upper	26	71	3
	Lower	31	67	2
06-10	Upper	23	73	4
	Lower	24	73	3
07-08	Upper	30	67	3
	Lower	32	65	3
08-12	Upper	27	71	4
	Lower	22	75	3
09-04	Upper	25	71	4
	Lower	28	68	4

TABLE 46. DENSITIES (PARTICLES/2,800 μm^2) OF TOTAL PARTICULATE MATTER AND FLY ASH ON VARIOUS POINTS OF BLACK OAK LEAVES COLLECTED AT SITE W5 DURING 1976

	Upper leaf body		Upper leaf vein		Lower leaf body		Lower leaf vein	
Collection date	Total grains	Fly ash	Total grains	Fly ash	Total grains	Fly ash	Total grains	Fly ash
05-20	8.7	2.8	0.25	0.10	1.4	0.75	1.1	0.40
06-10	14	4.9	5.5	1.4	5.0	3.2	2.4	0.95
07-08	22	7.2	1.4	0.35	8.1	4.0	5.2	2.1
08-12	17	6.0	6.3	1.5	13	6.3	1.6	0.60
09-09	15	5.0	6.0	1.6	15	8.0	9.6	3.4

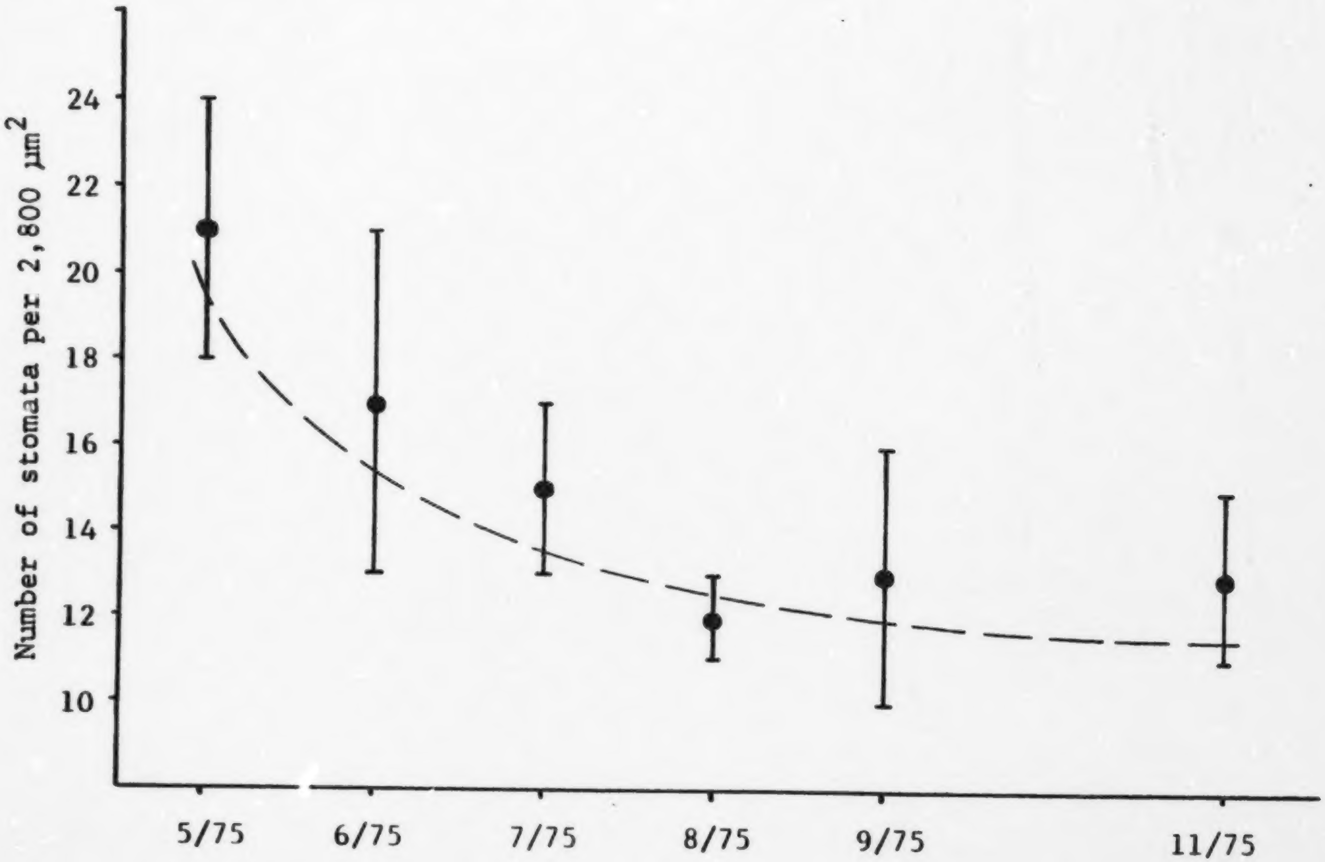


Figure 19. Stomatal density for black oak leaves collected at site W5 during 1976. The error bar represents one standard deviation.

veinal and non-veinal areas. As seen in Table 46, more ash collected on the upper surfaces during the early months than on the lower surfaces. As the leaves matured, the amount of ash on the lower sides was equal to or greater than that on the upper sides (Figure 20).

Ash collected by the veins on the upper and lower surfaces is quite variable in quantity. Although there tended to be high concentrations of particles on certain parts of a vein, many areas were void of particles entirely, whereas particles collected by the remainder of the leaf surfaces tended to be rather evenly dispersed over that surface. Little or no correlation existed between total grains and fly ash collected on either the upper or lower surfaces, but the data suggest that the veins might be more efficient collectors of ash compared to non-ash particles.

The size of particles collected by the leaves is considerably smaller and of a much narrower range than is found in the dust collectors or in material in the electrostatic precipitators at the generating station. Information concerning mean particle size for the four leaf areas from site W5 are presented in Table 47. The cut-off size of collection of particles appears to be 0.25 μm, which is considerably smaller than those seen elswhere, and generally the particles are < 5 μm. In the September sample, however, a number of large particles, up to 34 μm, also were found on leaf surfaces.

TABLE 47. MEAN GRAIN SIZE (μm) OF FLY ASH ON
BLACK OAK LEAVES DURING 1976

Date of collection	Upper leaf body	Upper leaf vein	Lower leaf body	Lower leaf vein
05-20	0.54 ± 0.46	1.12 ± 0.71	0.56 ± 0.36	1.06 ± 0.88
06-10	0.34 ± 0.33	0.88 ± 0.47	0.31 ± 0.28	1.00 ± 0.50
07-08	0.53 ± 0.48	1.42 ± 1.06	0.42 ± 0.39	1.22 ± 0.83
08-12	0.46 ± 0.42	0.50 ± 0.47	0.32 ± 0.36	0.75 ± 0.64
09-09	0.49 ± 0.31	2.42 ± 4.58	0.37 ± 0.35	1.56 ± 0.96

These results show that: 1) Aerosolic dust is deposited on leaf surfaces; and 2) a significant portion of the dust is fly ash. No damage or other visual effects were observed to result from the aerosolic dust or fly ash. The amount of fly ash increases continually through the growing season, indicating that wind and rain do not efficiently remove fly ash from leaves.

Seasonal Increase of Aerosolic Dust on Leaves

The results of the tracer studies showed that bioaccumultion of Sc by oak leaves was insignificant. The concentration of Sc in the oak leaves should therefore increase during the growing season if the concentration of

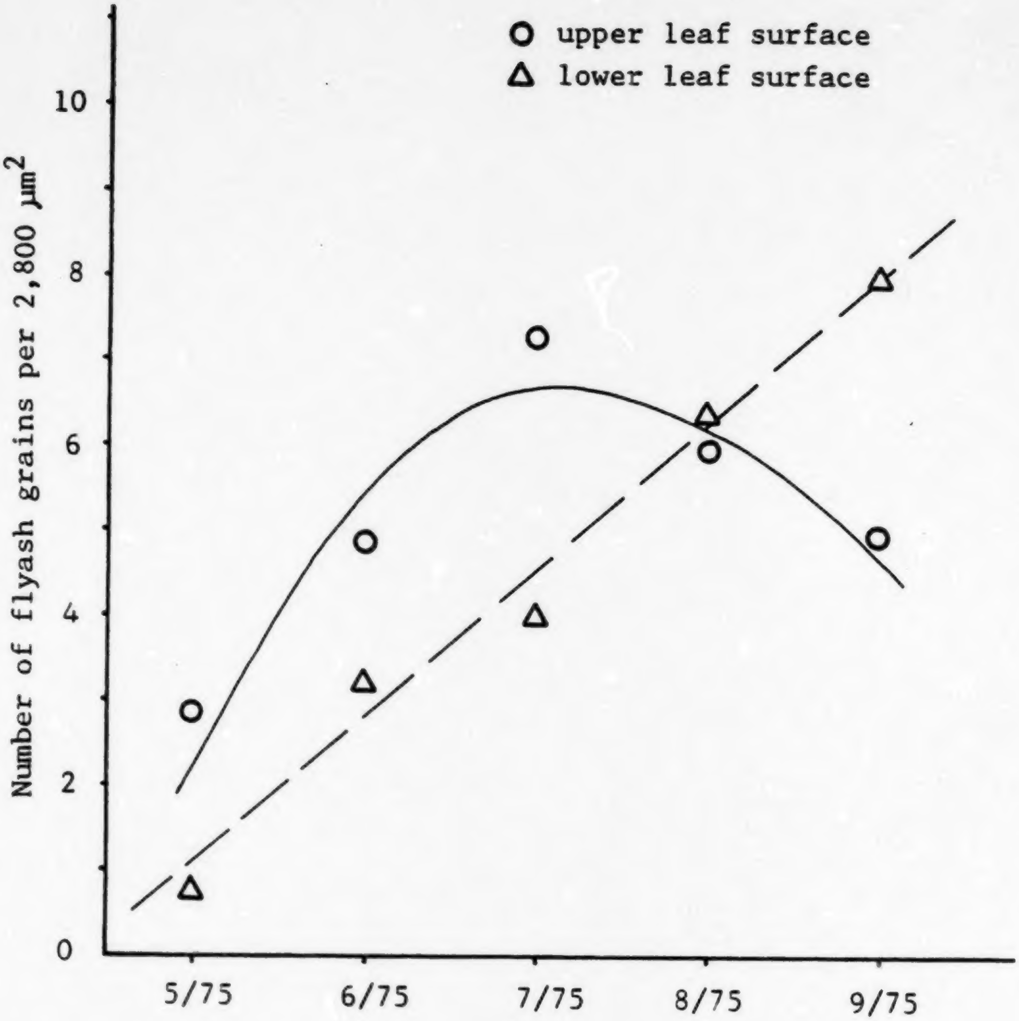


Figure 20. Density of fly ash grains on upper and lower surfaces of black oak leaves collected at site W5 during 1976.

aerosolic dust increases as shown by electron microscopy. Representative data are given in Figure 21 which show the concentration of Sc in washed samples of white oak leaves from three sites in 1976 as a function of stage of the growing season. Leaves from three sites had similar masses and apparently similar loadings of aerosolic dust as indicated by their nearly identical concentrations of Sc. The increase in concentration of Sc as a function of time is nearly identical to the increase in the number of fly ash grains as a function of time (Table 46). This provides clear evidence that measured concentrations of Sc in samples of oak leaves result from inorganic (dust) contamination.

Concentrations of Elements in Oak Leaves

Potentially Toxic Elements--

The concentrations of the potentially toxic trace elements of interest --As, Hg, Sb, Se, Th, and U--are low or below detection limits. This indicates the absence of any significant contamination of the sites, or influences from local soil anomalies, and the general ability of leaves to reject these elements. The concentrations of As and Hg for all but two samples are < 60 ng/g, which, when expressed on a wet weight basis, is < 10 ng/g. The wet weight concentrations of Sb are < 1 ng/g. Except for one sample, the concentrations of Sc are below detection limits. Concentrations of Se in trees reported in the literature suggest that they are < 50 ng/g on a dry weight basis. Thorium and U could not be detected. Concentrations of the remaining essential elements fall within reported ranges.

Effects of Aerosolic Dust on Elemental Composition--

Accepting the hypothesis that all Sc present in the oak leaves results from contamination by aerosolic dust, the proportion of elements contributed by aerosolic dust can be calculated by use of interelement ratios and elemental composition data for aerosolic dust (Table 44). The calculations are similar to those outlined for aquatic invertebrates. Results show that most of the Ba, Br, Ca, Cs, Cu, Hg, K, Rb, and Zn found in the leaves is indigenous while most of the La, Sb, Sc and Sm is due to inorganic contamination. The concentrations of As, Co, and Fe have significant contributions from each source.

Seasonal Variability--

The concentrations of elements in samples of washed and unwashed white and black oak leaves as a function of time for three sites are shown in Figures 22 and 23. The concentrations of most elements, especially those undergoing bioaccumulation, vary during leaf development in May and June, but are relatively constant after the leaves reach maturity (July through September). Elements that have important contributions from aerosolic dust tend to increase through the growing season.

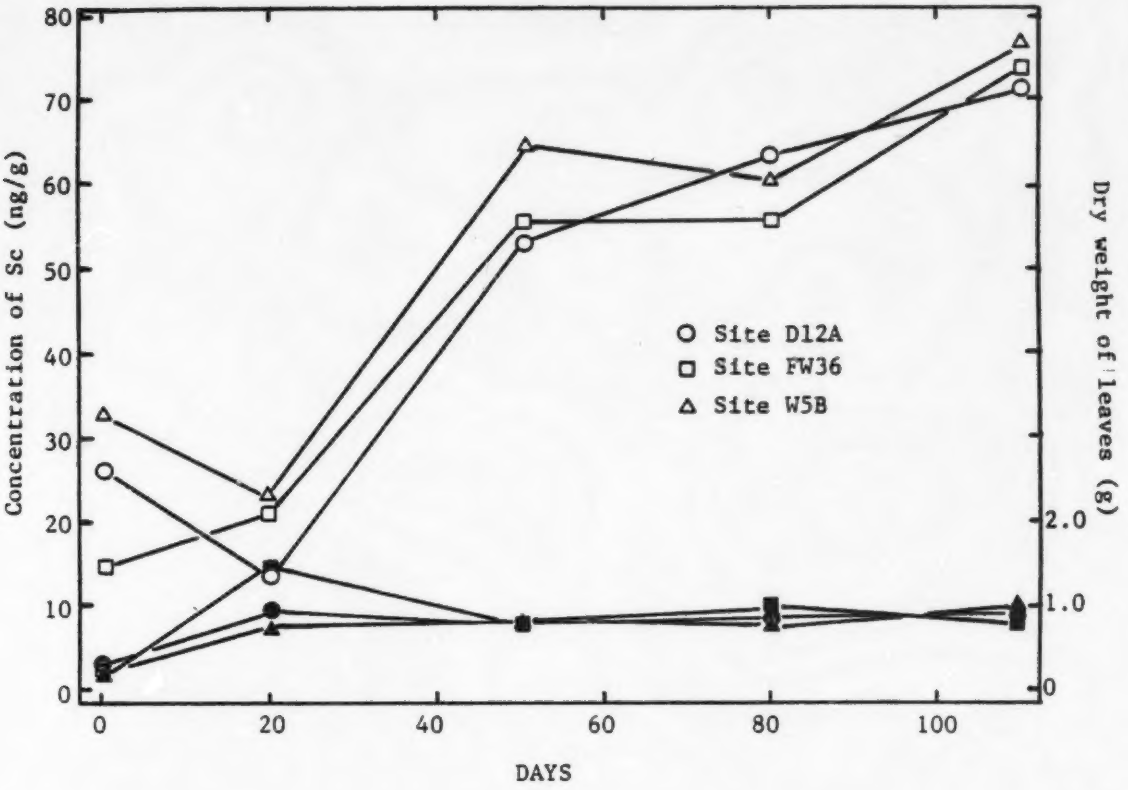


Figure 21. Concentration of Sc and average dry weight as a function of time for washed samples of white oak leaves from three sites in 1976.

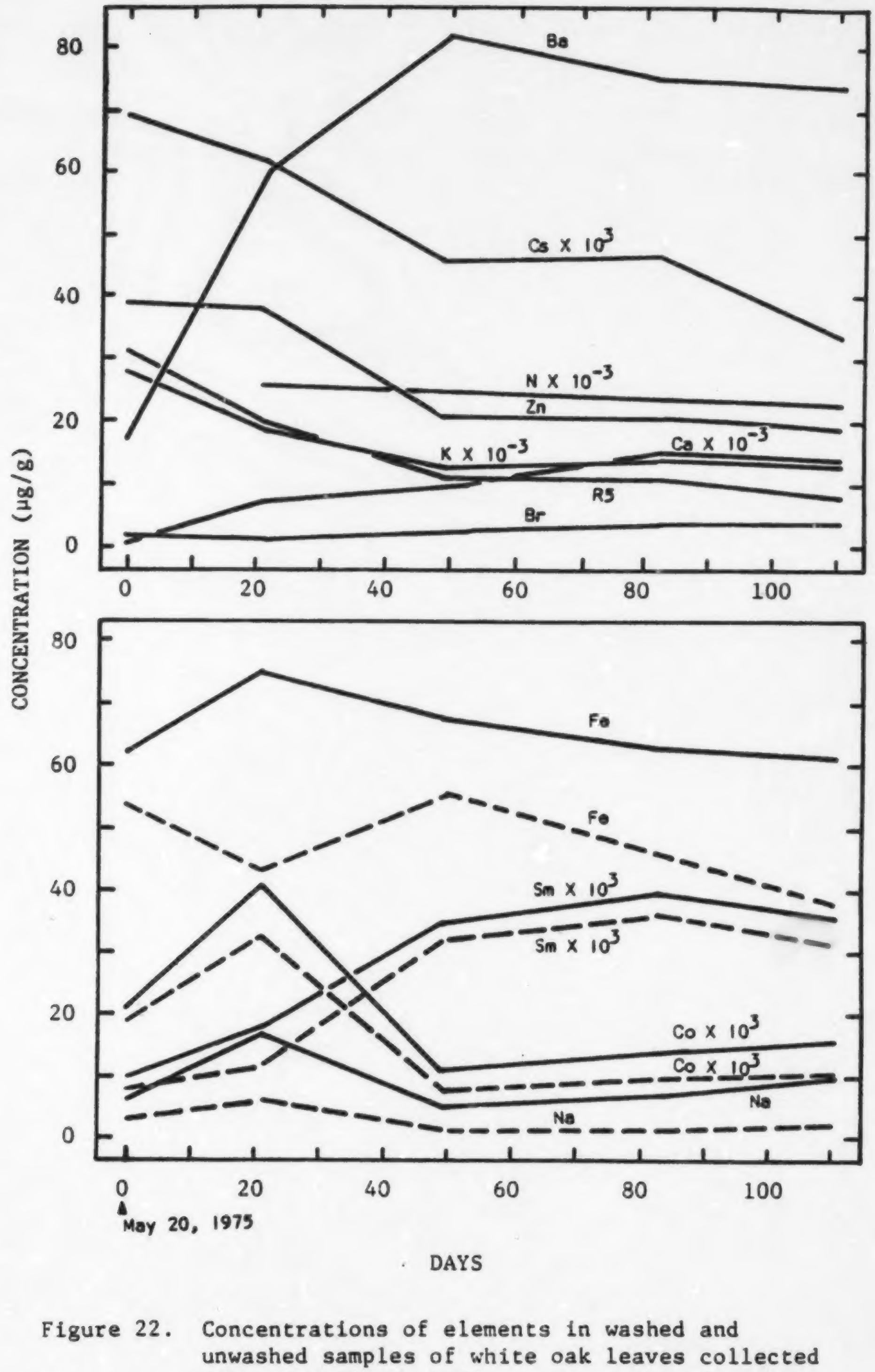


Figure 22. Concentrations of elements in washed and unwashed samples of white oak leaves collected from site D12 in 1975 as a function of time.

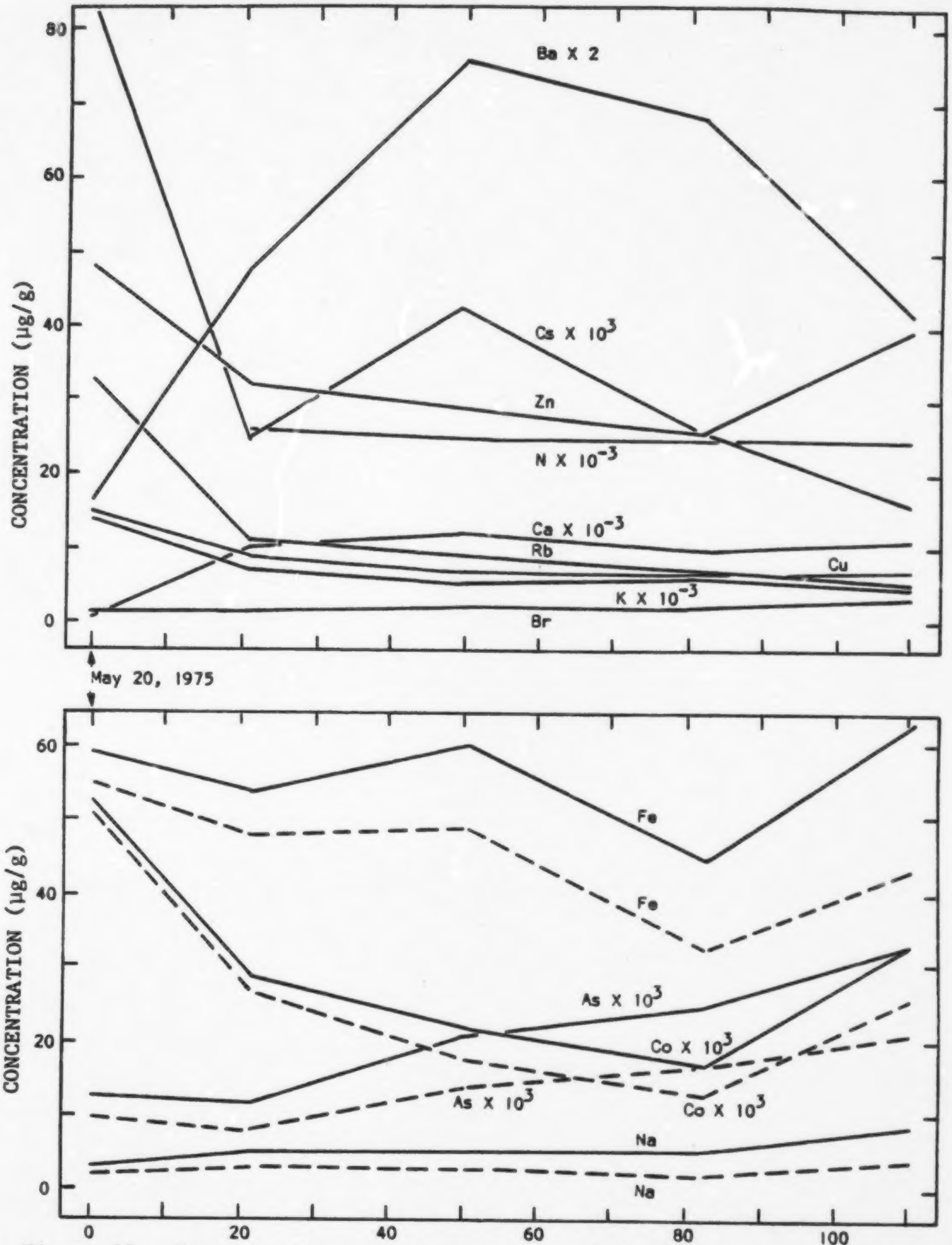


Figure 23. Concentrations of elements in washed and unwashed samples of white oak leaves collected from site W5 in 1975 as a function of time.

TABLE 48. CONCENTRATIONS (μg/g) OF ELEMENTS IN WASHED WHITE OAK LEAVES COLLECTED BEFORE AND AFTER START-UP OF THE STATION[a]

Element	9/14/73	9/17/74	9/09/74	9/09/76
		Site W5		
As	0.048 ± 0.002	0.041 ± 0.001	0.033 ± 0.001	0.032 ± 0.001
Ba	40 ± 3	69 ± 2	21 ± 1	54 ± 2
Cd	0.14 ± 0.03	---	0.13 ± 0.01	---
Hg	0.045 ± 0.003	0.045 ± 0.001	0.051 ± 0.001	0.037 ± 0.001
Sc	0.0090 ± 0.002	0.0082 ± 0.0003	0.0071 ± 0.0002	0.0077 ± 0.0003
Zn	36 ± 2	34 ± 1	40 ± 0.8	27 ± 0.8
		Site D12		
As	< 0.05	---	0.031 ± 0.004	0.022 ± 0.0007
Ba	88 ± 5	---	70 ± 2	---
Cd	---	---	0.29 ± 0.04	---
Hg	0.054 ± 0.004	---	0.048 ± 0.001	0.032 ± 0.001
Sc	0.010 ± 0.001	---	0.0052 ± 0.0004	0.0072 ± 0.003
Zn	48 ± 1	---	47 ± 1	34 ± 1
	6/11/74	6/10/75	6/10/76	
As	0.048 ± 0.005	0.012 ± 0.002	0.010 ± 0.001	
Ba	25 ± 2	24 ± 1	25 ± 0.8	
Cd	---	0.19 ± 0.02	---	
Hg	0.036 ± 0.007	0.036 ± 0.001	0.02 ± 0.001	
Sc	0.007 ± 0.001	0.0024 ± 0.0002	0.0023 ± 0.002	
Zn	25 ± 1	32 ± 0.6	26 ± 0.8	

[a] Analytical uncertainties represent one standard deviation based oncounting statistics.

Effects of the Columbia Generating Station

Only a few samples were collected prior to the start-up of the station in April 1975. Table 48 shows that the concentrations of all elements are nearly constant from year to year at each site. This is true for elements that: 1) Have high concentrations in the fly ash from the Columbia Generating Station, e.g., Ba; 2) are volatile, e.g., Hg; 3) are an essential nutrient, e.g., Zn; or 4) result from contamination by aerosolic dust, e.g., Sc. The effects of fly ash deposited on oak leaves cannot be detected in this study.

5. GENERAL DISCUSSION

Stack emissions from coal-fired electric generating stations consist of two principal components: gases and fly ash. Fly ash is made up of very small-sized particles that escape the electrostatic precipitators. In this study, fly ash was monitored to assess its dispersal in the environment and its impact on the biota around the generating station.

A multifaceted study of fly ash particles indicates that during the gaseous phase of combustion, these particles form a surface coating that is highly reactive. The surface enrichment of these particles cannot be measured by analysis of a total sample (bulk analysis). Previous assessments of the possible impacts have understated this potential by comparing the concentrations of components with the earth's crustal abundance. This type of comparison underestimates the availability of certain components which have been shown to be readily extractable. A comparison of surface analysis to bulk analysis shows concentrations (µg/g) of Pb of 2,700:620, of Th of 920:28; of Cr of 1,400:400; of Zn of 14,600:1,250, and of As of 1,500:600. Disposal or use of fly ash must be carefully evaluated with these surface properties in mind. This includes the recognition that some particles of fly ash are hollow and contain additional smaller particles, possessing the potential, in theory, for "timed release" effects which may not be observable until some future date.

Analysis shows that the concentrations of most of the trace elements found in this airborne fallout from the Columbia Generating Station are similar to those found in the soils of the area. One explanation for this finding could be that the sampling stations are too close to the plant; it appears that particulates in the plume from the stack are dispersed to much greater distances, possibly 30 or 50 km away. It is probable that most of the fly ash is coming from distant plants.

Of the aquatic organisms tested as indicators for monitoring ecosystem trace element fluxes, *Asellus racovitzai* and Odonata are the most suitable. The concentrations of Ba, Cr, Sc, and possibly Sb are higher in specimens of these organisms exposed to the ash effluent than in control specimens. These increases cannot be attributed to seasonal variability, sample contamination, or differences in specimen size and are therefore thought to result from exposure of the organisms to ash effluent. Corixidae, *Dineutus* spp., *Gammarus* sp., and *Hyallela azteca* are less useful indicator organisms. The extent to which *Dineutus* spp. specimens reflect conditions at the site of collection is uncertain due to their high mobility. *Hyallela azteca* was not found in the ashpit drain after the start of operations, possibily due to exposure to the ash effluent. The concentrations of many elements of environmental interest (e.g., Ba, Cr, Sb, and Se) were generally lower in

Corixidae and *H. azteca* than in the *A. racovitzai* and Odonata specimens collected from the same sites. The differences in gross element concentrations may be due to differences in feeding habits, exoskeleton permeability, and ability to excrete a given element. Differences in element concentrations between specimens exposed to the ash effluent and controls could not be established for Corixidae and *H. azteca*.

Concentrations of rare earth elements and Co, Fe, Hf, and Sc were higher and more variable in the benthic arthropods than in the *Dineutus* spp. Concentrations of these elements in the benthic organisms were significantly correlated with Sc concentrations. High organism Sc concentrations result from inorganic contamination; consequently concentrations of Co, Fe, and Hf in organism tissue can only be determined if some method of correcting for sample contamination is employed. To this end, it is important to analyze the sediment environment from which the organisms were collected.

The contribution of gut contents to whole organism elemental composition is important for some elements in *A. racovitzai* and presumably in other taxons. Before elemental composition in whole organisms can be compared accurately, specimens with empty guts must be analyzed, or a correction procedure must be used to show that the gut contents do not significantly affect results.

Insufficient control samples preclude statistical evaluation of the effects of the ash effluent on trace element tissue levels in frogs. Concentrations of Ba in skin samples were higher for specimens exposed to the ash effluent than for controls.

Potential effects of fly ash from the Columbia Generating Station or other aerosolic dust on the concentrations of elements in oak leaves could not be detected. Grains of fly ash and other aerosolic dust are deposited on oak leaves. Their concentration on the leaf surfaces increases through the growing season. This accumulation of dust causes concentrations of some elements in the samples to increase during the growing season, but all evidence indicates that these elements do not undergo bioaccumulation in leaves.

Concentrations of elements in oak leaves change rapidly during leaf development in May and June, but are relatively constant thereafter. The concentration of elements in oak leaves are similar from year to year and from site to site for any given stage of the growing season. The concentration of Hg--emitted as a gas from generating station stacks--is < 60 ng/g in dry oak leaves. The concentrations of this element are almost identical for all samples, including those collected before and after start-up of the station.

Microscopic examination of leaves can be used to identity particles in aerosolic dust that is being removed from the atmosphere. Data collected serve as a baseline for future studies evaluating the additional loading of the atmosphere with aerosolic dust as new coal-fired generating stations come on line.

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